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Determination of Trace Metal Concentrations in soil of Tafila Solid Waste Disposal Site, Jordan

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Determination of trace metal concentrations in soil of Tafila solid waste disposal site, Jordan

استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء.

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Dedication

To My Father

To My Dearest Mother

To My sisters and brothers that were the perfume of my morning

To My teacher who taught me the right way with the right vision

To My colleagues that are waiting the time to come to do what I am to harvest.

To the morning, to the sun that rises every single day to tell me that there is a time to succeed.

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Abbreviations

EC	Electrical Conductivity
EF	Enrichment Factor
CRM	Certified reference material
GIS	Geographical Information Systems
GPS	Global Positioning System
AAS	Atomic Absorption Spectrometer
Ppm	Parts per million
LOD	Limit of Detection
LOQ	Limit of Quantitation
RSD	Relative Standard Deviation
TOC	Total organic carbon
r^2	Correlation coefficient
USDA	US Department of Agriculture
SD	Standard deviation
FAAS	Flame Atomic absorption spectrometer

Abstract

Determination of Trace Metal Concentrations in Soil of Tafila Solid Waste Disposal Site, Jordan

Maha Ali Al-Shabatat

Mut'ah University, 2013

The present study aimed to determine the concentration of trace metals and their distribution patterns in a soil profile of the Tafila solid waste disposal site. The analytical method validation included an optimization of the microwave digestion method using an acids mixture for analysis of trace metal concentrations in soil samples and it was performed using a certified reference material (CRM 141r).

Soil samples were collected during the winter on December 2012 from the investigated solid waste disposal site which located 35 km southern plateau of Tafila governorate. In order to investigate the impacts of solid waste disposal on soil beneath, the samples were obtained at three soil depths 0-20, 20-40, and, 40-60 cm. The following metals were analyzed namely: Zn, Ni, Pb, Cu, Co, and Fe using atomic absorption spectroscopy (AAS). The physical and chemical soil properties, which believed to affect trace metals mobility in soil of the study area, were examined using pH, TOC %, EC, $CaCO_3$ %, and soil texture.

The pH values was found within the normal Jordanian soil range which is characterized by alkaline pH due to presence of high carbonate buffering. TOC percent found to be affected by solid and liquid wastes disposal mainly at the top layers due to recent waste disposal activities. The soil EC results showed that some of the samples collected from the upper soil layer were saline due to heavy waste disposal and the soil texture was characterized as loamy.

The concentration levels of trace metals for the investigated site have been classified as a polluted site according to the typical range of trace elements in non-polluted soil. Finally, the enrichment factor calculations showed that Cu was high enriched compared to other elements. The statistical analysis of the results using the Principle Component Analysis (PCA) showed that the solid wastes disposal may be the main source of trace metals in study area.

الملخص

تحديد تركيز بعض العناصر الثقيلة وتوزيعها على سطوح التربة في مكب النفايات الصلبه في محافظه الطفيله

مها علي الشباطات

جامعة مؤتة، 2013

هدفت الدراسة الحالية لتحديد تركيز العناصر الثقيلة وتوزيعها على سطوح التربة في مكب النفايات الصلبة الواقع في محافظه الطفيلة، حيث تم القيام بتحديد أفضل طريقه لهضم العينات باستخدام جهاز المايكرويف وخليط من الأحماض، كما تم كذلك فحص طريقه التحليل ومدى فاعليتها باستخدام المواد المرجعية (CRM 141r) لتحديد تراكيز العناصر الثقيلة في تربة المناطق الجافة وشبة الجافة وحساب مدى كفاءة طريقة التحليل المتبعة.

لقد تم جمع عينات من التربة خلال شهر كانون الأول في شتاء عام 2012 من مكب النفايات الصلبة والذي يقع على بعد 35 كم من الجزء الجنوبي لمحافظه الطفيلة، من أجل معرفه تأثير مكب النفايات الصلبة على طبقات التربة، والعينات تم أخذها عند ثلاثة أعماق تراوحت ما بين (60-40 ,40-20 ,20-0) سم للعناصر التالية : Zn, Ni, pb, Cu, Co, (Fe) باستخدام جهاز طيف الامتصاص الذري. والخصائص الفيزيائية والكيميائية والتي يعتقد بأنها تؤثر على حركه العناصر الثقيلة في التربة في هذه الدراسة مثل: درجه الحموضة، الايصالية الكهربائية، المادة العضوية، نسبه كربونات الكالسيوم، والنسجه للتربة.

وقد وجدت قيم درجه الحموضة لعينات التربة هي ضمن المدى الطبيعي للترب الأردنية حيث إنها ترب قاعدية والسبب في ذلك وجود محتوى عالي من كربونات الكالسيوم، أما بالنسبة لمجموع المادة العضوية فقد وجدت متأثرة بالنفايات الصلبة والسائلة وخاصة في الطبقة العليا الملامسه للنفايات الحديثة. أما بالنسبة للايصالية الكهربائية لبعض العينات المأخوذة من الطبقات العليا للتربه فقد وجدت بأنها مالحة والسبب في ذلك يعود إلى النفايات الصلبة، وتميز نوع النسجه بالتربة اللوميه.

إن مستويات التلوث للعناصر الثقيلة في منطقه الدراسة يمكن تصنيفها بأنها منطقه ملوثه بالرجوع إلى المقياس الطبيعي للعناصر الثقيلة في التربة غير الملوثة. وفي الختام، أظهرت حسابات عامل الإثراء بأن عنصر الزنك أكثر إثراء بالمقارنة مع غيره من العناصر الأخرى ، وقد أوضح التحليل الإحصائي للنتائج باستخدام برمجيه التحليل PCA بأن النفايات الصلبة هي المصدر الرئيسي لتلوث منطقه الدراسة بالعناصر الثقيلة.

Chapter One
Theoretical Background

1.1. Conception of waste disposal:

Landfilling has been used for many years as the most common mean for solid waste disposal generated by different communities (Abu Qdais, 2007), and it is the most commonly used method for solid waste disposal in Jordan. Landfilling is an important source of pollution, which can be displayed through analysis of data for climatic conditions, hydrology and geology of the country. The migration of leachate from the landfill body into the surrounding environment present a serious environmental concern, which include soil, atmospheric and water pollution. When leachate leaves the landfill and reaches soil and water resources, it may cause soil pollution, surface and ground water pollution. The quantity of leachate generated in a landfill depends on the climate in which the landfill is situated, as well as the type of waste and the water content (Abu Qdais, 2007). The migration of pollutants in the soil is dependent on several factors such as pH, moisture content , and soil texture (Dube et al. 2001).

1.2. Objectives of study

The objectives of the present study are:

1. Validation of analytical procedure for the determination of trace metals in semiarid to arid soil in Jordan using acid microwave digestion and atomic absorption spectrometry (AAS).
2. Assessing the trace metals pollution in solid waste disposal site and compare the obtained concentrations with control areas.
3. Characterizing the distribution pattern of trace metals with respect to the soil depth and its potential impact on groundwater resources.
4. Studying the distribution pattern of trace metals in the investigated area and evaluate their leachability.

1.3. Solid waste in Jordan:

The solid waste generation in Jordan can be attributed to the following sources: municipal residential waste, commercial waste, bio-waste from wastewater treatment plants, industrial waste, institutional waste and agricultural waste. The average waste generation is in the range of 0.34 to 1.07 kg/Capita/day (average 0.91 kg/Capita/day) (Chopra et al. 2001). The composition of solid waste in Jordan is consisted mainly of organic matter 52%, paper 13 %, metal 1%, glass 3%, plastic 17 % , and others 14% (SWEEP, 2010) as shown in Figure 1.1. However, the composition of solid waste in Tafila governorate was estimated as kitchen residue 62%, paper 9 %, plastics 4 %, agriculture residues 13 %, glass 3 %, metal 3%, textile 4 %, and other 2 %, Figure 1.2.

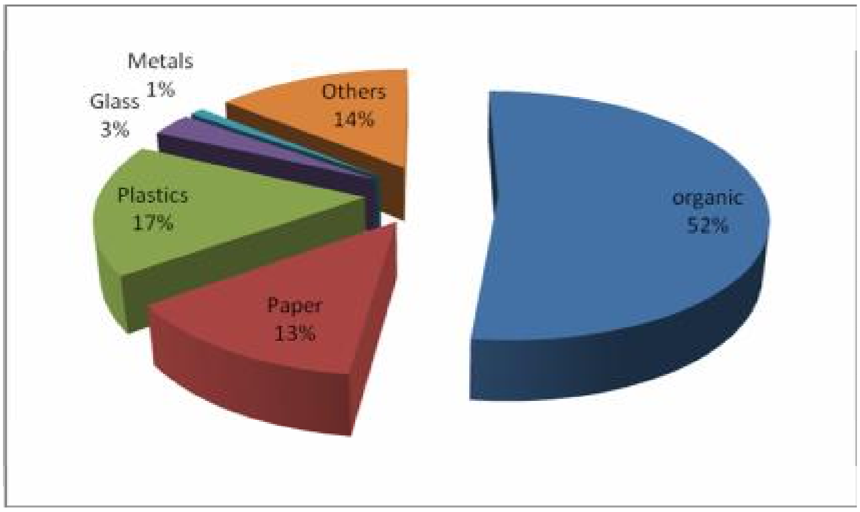


Figure (1.1)
The Physical compositions of solid waste in Jordan (SWEEP, 2010).

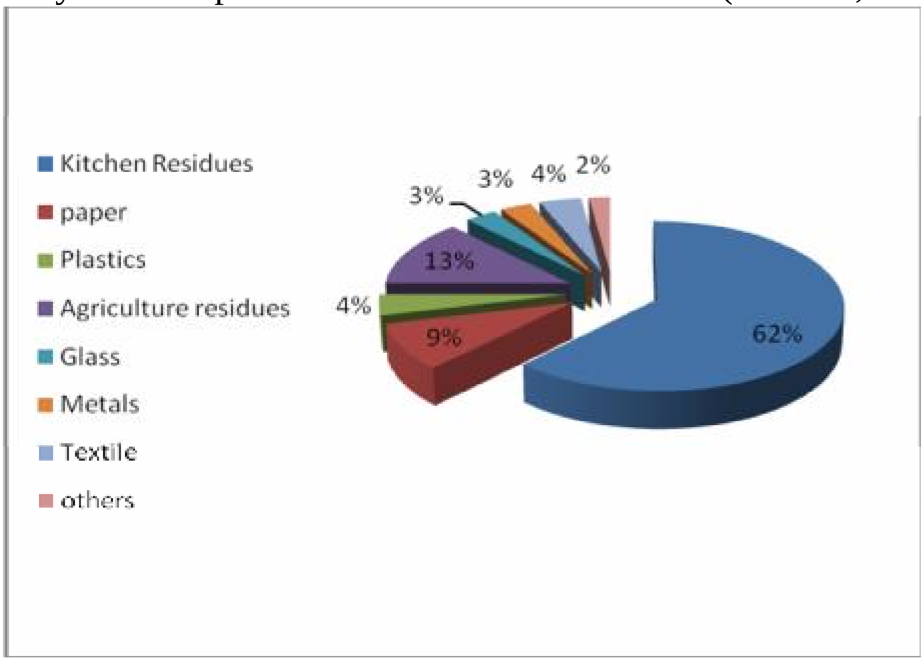


Figure (1.2)
The physical compositions of solid waste disposal in Tafila.

Solid waste generation in different Arab and Western countries are presented in Table 1.1. The general trend is that an increase in the per capita income results in a higher rate of solid waste generation (Al-Yousfi, 2004). Still, comparing with other Arab and some of the industrial countries all over the world, the solid waste generation rate in Jordan is high as shown in Tables 1.1 and 1.2.

Table (1.1)
Solid wastes generation in some Arab countries (Al-Yousfi, 2004)

Country	**Municipal waste** Kg/Capita/day	**County**	**Municipal waste** Kg/Capita/day
Bahrain	1.60	Qatar	1.30
Egypt	1.20	Saudi Arabia	1.30
Jordan	0.90	Syria	0.50
Kuwait	1.80	Tunis	0.60
Oman	0.70	UAE	1.20
Morocco	0.33	Yemen	0.45

Table (1.2)
Solid wastes generation in industrial countries (Al-Yousfi, 2004)

Country	**Municipal waste** Kg/Capita/day	**County**	**Municipal waste** Kg/Capita/day
Canada	1.65	Germany	0.80
Denmark	1.32	Japan	1.26
Finland	0.47	Netherlands	1.04
France	0.90	USA	1.98

1.4. Tafila solid waste disposal site

Tafila is a rural centre in the southern part of Jordan, with a municipal population of 80,000 inhabitants; the Tafila governorate consists of four municipalities. The solid waste generation in Tafila city which is the main municipality with a population of 49,000 inhabitants is around 40-45 tons/day or 0.9 kg/capita/day, Figures 1.3 and 1.4. The solid waste is collected by compacter vehicles; these vehicles are owned and operated by Tafila Municipality. Each compacter has its crew which is usually two employees and a driver. Each round of service for each compacter takes around 5 hours; they start to collect waste from the containers which are distributed all over the entire city early morning about 5 am, but another round usually for markets, shops, and poultry industry in the evening. After finishing each round the compactors transport their load to the solid waste disposal site directly. However, before the covering process some scavenging is done inside the dumping site by the employees working there. In the past municipality used to rent the dump site to private contractors. The contactors dug up the waste and collected the recyclable materials then loaded it on trucks and sold it to interested companies.



Figure (1.3)
Tafila solid waste disposal site



Figure (1.4)
Tafila solid waste disposal site (cesspools)

1.5. Geology and geomorphology of Tafila solid waste disposal site

The Al-Hisa phosphorite formation (campanian – maestrichant) cropping out (50 m) and marked by two prominent beds of dark grey chert, and by marly limestone and phosphite, also Muwaqqar chalk formation (upper maestrichtain) Paleocene in age crops out in the area (Natural Resources Authority,1993-1994). Geology structure is reflected on the morphology of the area. The main morphology shaped as a watershed which divides the area into water channel (wadies) that are running NW-SE where the wadi drained towards wadi Al-Hisa and to the Dead Sea basin. Whatever shallow and wide wadies at the solid waste disposal site are shaping, the general structural feature controlled the drainage

development in the area, and for this reason the infiltration of the heavy metals might effect on the aquifer (Bender, 1974).

1.6 Literature Review:

Many studies had been conducted to investigate the trace heavy metals pollution in soil worldwide, the trace heavy metal concentrations in Russiefeh site-Zarqa landfill, Akaider site-Irbid landfill, and Ghabawi site-Amman landfill were found that the concentration of Cu in Russiefeh site-Zarqa landfill (5 – 808 mg kg^{-1}), Akaider site-Irbid landfill (46.6 – 1,048 mg kg^{-1}) and Ghabawi site-Amman landfill (0- 1.06 mg kg^{-1}), also, the concentrations of Ni in Russiefeh site-Zarqa landfill (33.3 – 233.3 mg kg^{-1}), Akaider site-Irbid landfill (123.3 – 1,115 mg kg^{-1}) and Ghabawi site-Amman landfill (90-713.3 mg kg^{-1}). The Co, Zn, and Pb in the three landfills leachates exhibit no significant threat. Furthermore, Ghabawi and Akaider sites showed very high concentrations of Ni according US Environmental Protection Agency (Abu-Daabes et al. 2013).

The mean concentration of trace heavy metals in soil samples in Akaider landfill site was found :(Zn) 15,000 – 43,500 mg kg^{-1}, (Pb) 31.66 – 283.3 mg kg^{-1}, (Cu) 7.31 – 3,208 mg kg^{-1}, and (Fe) 25 – 3,206 mg kg^{-1}. Akaider landfill leachate constitutes cause a serious threat to the local aquifers in the Yarmouk Basin (Aljaradin and Person, 2012). There are many possible sources for groundwater contamination, including landfills, septic tanks and cesspools, domestic and industrial effluents, leaky sewage system and gasoline stations, Areas near landfills have a greater possibility of groundwater contamination because of the potential pollution source of leachate direct mitigation. During the last 20 years, many evidences for groundwater contamination have been presented especially in northern part of Jordan (El-Naqa et al. 2006), a gradual increase of element concentrations has been reported in the groundwater wells around the Akaider landfill starting from 1985 (Jawad et al. 1998).

In Old Karak Solid Waste Disposal Site (Jiries et al. 1994), a study found that the concentration of trace heavy metals samples were (Zn) 8,433 – 21,166 mg kg^{-1}, (Pb) 3,083 – 63,333 mg kg^{-1} , and (Cu) 3,083 – 6,550 mg kg^{-1}.

Solid waste samples were collected in the National Capital Territory (NCT) of Delhi**.** Solid waste samples were digested using aqua-regia and HF in air tight Teflon bombs for the quantitative analysis of heavy metals (Hg, Pb, Cd, Mn, Fe, Ni, Cu and Zn) by atomic absorption spectrophotometer**.** The result obtained showed metal concentration to be in the range of Hg 0.42–2.3, Pb 23–530, Cd 0.14–224, Mn 494–19 964, Fe 684–233 119; Ni 192–1534, Cu 3065–10144 and Zn 116–23321 (mg kg^{-1}) (Moturi et al. 2004)**.**

In the North Greece soil samples of a closed landfill located northwest of Thessaloniki were obtained by drilling in different depths (2.5–17.5 cm). Then they were analyzed by atomic absorption spectrophotometer for Cd, Cr, Cu, Ni, Pb and Zn. The chemical analysis showed that the metal values varied over a wide range: from 0.50 to 18.75 mg kg^{-1} for Cd, 3.78–171.88 mg kg^{-1} for Cr, 8.13–356.25 mg kg^{-1} for Cu, 5.63–63.65 mg kg^{-1} for Ni, 2.50–92.50 mg kg^{-1} for Pb and 6.38–343.65 mg kg^{-1} for Zn. The area is heavily industrialized; the presented results indicated that local industries have not constituted an extensive metal pollution source for the site (Kasassi et al. 2008).

1.7. Heavy metals

The trace heavy metals constitute a very heterogeneous group of elements widely varied in their chemical properties and biological functions. "Heavy metals" defined as commonly held for those metals, which have specific weights more than 5g cm^{-3} (Raikwar et al. 2008). Heavy metals are kept under environmental pollutant category due to their toxic effects in plants, human, and food. Some of the heavy metals such as arsenic (As), Cadmium (Cd), Lead (Pb), Mercury (Hg) are cumulative poison.

Soils become contaminated by the accumulation of metals and metalloids through emissions from the rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition (Khan et al. 2008).

Soils are the major sink for heavy metals released into the environment by anthropogenic activities and unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation (Kirpichtchikova et al. 2006), and their total concentrations in soils persist for a long time after their introduction (Adriano, 2003).

1.7.1. Sources of heavy metals

Heavy metals are natural constituents of the earth's crust. They are tend to accumulate in soils. The metals enter to environmental region to soil due to natural processes and anthropogenic activity. Table 1.3 summarizes the sources of some heavy metals contaminants in environment (Makepeace et al. 1995).

1.7.2 Classification of heavy metal

Heavy metals can be classified into four major groups on their health importance.

Essential: Cu, Zn, Co, Cr, Mn and Fe. These metals also called micronutrients (Reeves and Baker, 2000) and are toxic when taken in excess (Monni et al. 2000; Blaylock and Huang 2000). The toxic limit and recommended or safe intake of heavy metal for human health were reported by Oliver (1997).

Non essential: Ba, Al, Li and Zr

Less toxic: Sn and Ni

Highly toxic: Hg, and Cd.

Heavy metals are also called trace element due to their presence in trace amount not exceeding (10 mg kg^{-1}) or in ultratrace (1µg kg^{-1}) in the environmental matrices.

Table (1.3)

Sources of some heavy metals contaminants

Elemen	Typical Sources
Copper	Wear of tires and brake linings, combustion of lubricating Oils, metal – finishing industrial emissions, agriculture use fertilizers and pesticides, and corrosion of galvanized metals.
Lead	Emissions from gasoline- powered vehicles , gasoline Additives, Mining and smelting, iron and steel industry, refineries, paint industry, plumbing, battery Pb-metal–oxyanion manufacture, refuse disposal/landfills, pesticides, scrapheap's
Nickel	Corrosion of welded metal plating, wear of moving parts in engines, Electroplating and alloy manufacturing , activity of smelters , food Production, steel industry .
Zinc	Wear from tyres, brake pads, combustion of lubrication oils, activity Of smelters, corrosion of building materials and metal objects.
Cobalt	Manufacture of dyes, colours of plastics, leather, manufacture of Battery, printing ink
Iron	Welding, steel factories, heavy traffic, mining dust, Fertilizers industries and coloring, most of mechanical maintenance works.

1.7.3. Toxicity of heavy metals

Heavy metals pollution of soil may pose risks and hazards to humans and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems (McLaughlin, 2000).

1-Lead:

Lead can cause serious injury to the brain, nervous system, red blood cells, and kidneys (Wuana and Okieimen, 2011), it was found that various effects occur over a broad range of doses, with the developing young and

infants being more sensitive than adults. Lead poisoning, which is so severe as to cause evident illness, is now very rare. Lead performs no known essential function in the human body, it can merely do harm after uptake from food, air, or water. Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains.

2-Zinc:

Zinc has low toxicity to man compared to other metals but prolonged consumption of large doses can result in some health complication such as a fatigue, dizziness, and neutropenia, zinc is toxic to some aquatic organisms such as fish (Sparks ,2005).

3-Copper:

Copper is one among some heavy metals, which are essential to life but could be toxic at elevated levels. It is toxic at low concentration in water and known to cause brain damage in mammals (Nriagu,1988).

4-Nickel:

Nickel is an element that occurs in the environment only at very low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer (Franzbau et al. 1989).

5-Iron:

Iron also accumulates in the pancreas, spleen, and liver, iron overload is clearly associated with carcinogenesis which including esophageal, skin melanoma, and acute myeloid leukemia (Huang, 2003).

Chapter Two
Materials and Methods

2.1 Study Area

The study area was the Municipal Solid Waste Disposal site located in the southern part of Tafila governorate between 30° 44' 43" latitude and 35° 49' 33" longitude in Jordan, Figure 2.1. The site is an active disposal site which collects the cesspools wastewater and solid waste from Tafila City and its property since 1990.

The Tafila solid waste disposal site occupies 455,000 m^2 , it was established by Tafila municipality in 1990. The site receives around 65 tons of solid waste daily. Selection of individual solid waste is executed manually by scavengers (waste pickers) and the remainder is dumped and covered on the surface by 50 cm of soil layer. The average composition of solid waste was estimated as kitchen residue 62%, paper 9 %, plastics 4 %, agriculture residues 13 %, glass 3 %, metal 3%, textile 4 %, others 2 % (Tafila Solid Waste Disposal Files, 2012).

The study area is classified as an arid to semiarid region. It has predominantly Mediterranean climate that characterized by hot-dry summer and cold-wet winter. The temperature exhibits large seasonal and diurnal variation. The annual precipitation resulting largely from orographic effects that decreases rapidly eastwards from over 250 mm in the Tafila Metrology Station to less than 50 mm in the Ma'an station. More frequently seasonal mean temperatures vary from 6 °C in January to 22°C in July, reaching a maximum of 38.5°C in summer and a minimum of -4°C in winter with an average temperature of 22°C in summer and 8°C in winter (Howard Humphreys and Parteners, 1994). The investigated area is about 900-1300 m above the sea level (Metrology Station of Tafila, 2012).

The average daily wind speed in Jurf Al-Darawish is 18.86 Km / h , the site is mainly affected with northest – western wind (Metrology Station of Tafila, 2012).

The site was located in the rolling and rounded a limestone plateau with phosphorite formation with beds of dark grey chert and marly (Campanian–maestrichart) (Bender, 1974).

2.2 Samples collection

The sampling area was divided as an array of 12 column and 7 rows. The Global Positioning System (GPS) coupled with Geographical Information Systems (GIS) were used to locate sampling points in the field during the sampling activity. The GPS was used to establish the boundaries of the study area.

A total of 51 soil samples were collected from Tafila solid waste disposal site at three depths, 0-20 cm, 20-40 cm, and 40-60 cm using a manual auger. In addition 9 samples from reference remote site. The samples were selected based on dominant dumping activities as follows: soil samples that are affected by wastewater effluents discharge were collected from five sites, each site was sampled at three depths (0-20 cm, 20-40 cm, and 40-60 cm). Additionally, fifteen soil samples were collected at three depths (0-20 cm, 20-40 cm, and 40-60 cm) from the solid waste disposal sites that are affected by heavy solid waste dumping activities. Furthermore, thirty one soil samples were collected through the solid waste disposal to cover the whole investigated area. Finally, nine control remote soil samples were collected from areas located far away from the dumping site and not affected by any solid waste dumping activities, these samples were collected also at three depths: 0-20 cm, 20-40 cm, and 40-60 cm. Each soil sample was collected from an area of 5 m^2 and pooled together to get a representative sample. Stones and foreign objects were removed by hand and soil samples kept in plastic bags at room temperature.

2.3. Sample characterization:

2.3.1 Sample pre- treatment

To assure sample stability and homogeneity, the collected soil samples were dried and ground using a ceramic mortar with pestle. Then they were sieved through 85 µm (mesh 200) using a stainless steel sieve and stored refrigerated in plastic bags for subsequent sample preparation, microwave digestion and further analysis.

2.3.2 pH and Electrical Conductivity (EC)

The soil pH values were determined by shaking a 1:5 (w/w) ratio of soil and deionized water, the mixture was homogenized for 6 h using a horizontal shaker before measurement with a pH–meter model HI 254 (ORP Meter®, Germany).Electrical conductivity was measured in a saturated soil extract using an EC-meter model LF 750 (WTW®, Weilheim, Germany).

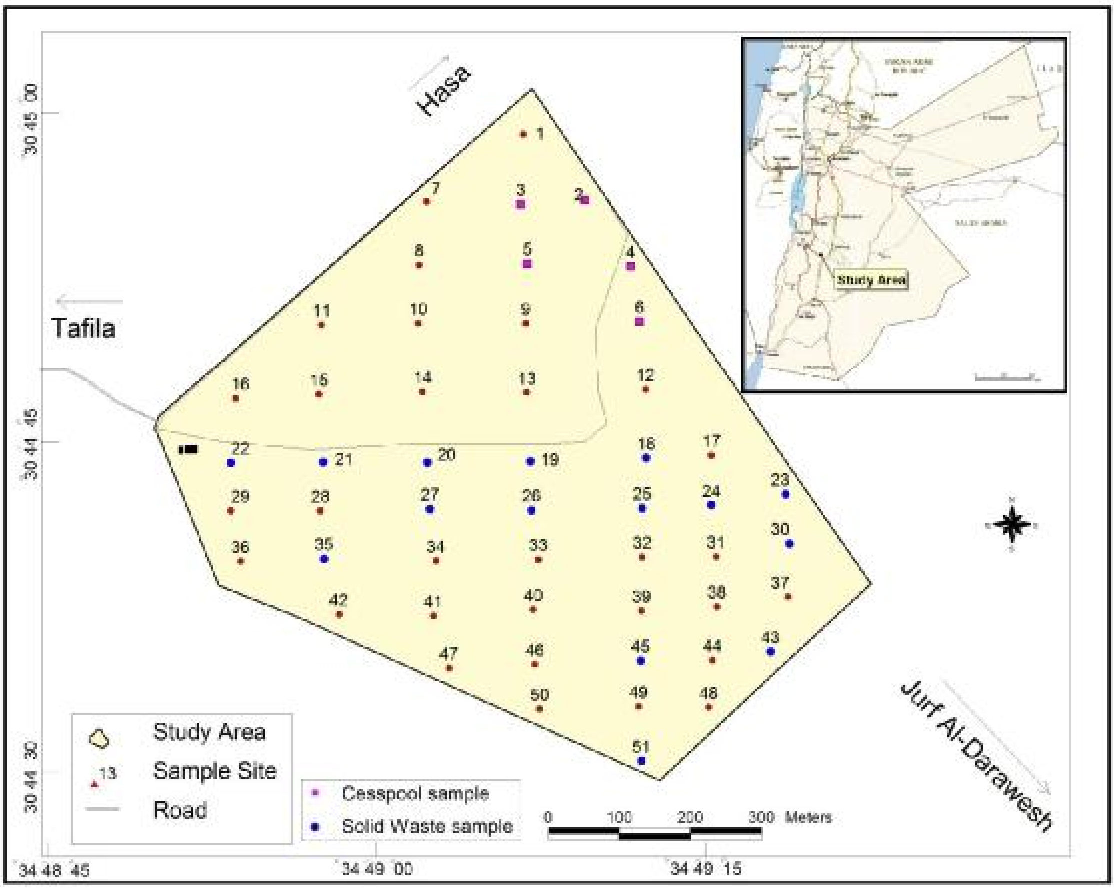


Figure (2.1)
location map of sampling sites of the Tafila solid waste disposal site

2.3.3. Calcium carbonate content

The calcium carbonate content ($CaCO_3$%) of 18 samples was determined by a rapid titration method as reported in (Bashour et al. 2007). To 5.0 g of oven dried and fine grained soil, 100 mL of 1M HCl was added. The mixture was boiled for 5 minutes and then cooled to room temperature, and the mixture was filtered. Then a 10 mL of filtrate was titrated with standardized 0.5 *M* sodium hydroxide (NaOH) to the phenolphthalein indicator endpoint. The $CaCO_3$% was calculated according to the following formula:

$$\text{CaCO3\%} = \frac{[(\text{mL HCl} \times 1\text{ M}) - (\text{ml NaOH} \times 0.5\text{ M})] \times (\text{vol.HCl}(100)]}{(\text{vol.filterate aliquot}) \times (100/1000 \times 2) \times (100\text{g}/\text{mol})/(\text{wt.of soil g})}$$

$$\text{CaCO3\%} = [(10 \times 1) - (\text{mL NaOH} \times 0.5\text{M}) \times 10]$$

2.3.4. Total Organic Carbon (TOC %)

Soils contain a large variety of organic material ranging from simple sugars and carbohydrates to more complex proteins, fats, waxes, and organic acid. Total organic carbon was determined by Walkley – black's

wet oxidation method, this procedure is simple, rapid, and has minimal equipment needs (Nelson and Sommers, 1996).

The total organic carbon (TOC %) was determined using the wet oxidation method according to Walkley - Blacks method (Baruah and Bathakur, 1997).To 0.5-1.0 g of oven dried and fine– grained soil, 10 ml of 1 M $K_2Cr_2O_7$ and 20 ml of concentrated sulfuric acid (H_2SO_4) were added. The mixture was gently shaken and allowed to stand for 30 min until completion of the oxidation reduction reaction. The mixture was diluted with 200 ml of distilled water, and then 10 ml of 85 % phosphoric acid (H_3PO_4) and 1 ml of diphenylamine indicator. Finally the mixture was back titrated against 0.5 M ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2.6H_2O$), until violet a color was observed. A blank titration was carried out in the similar way using all reagent except the soil, and then TOC % was calculated according to the following formula:

$$TOC \% = (B-S) \times 0.5 \times 0.003 \times (100/W) \times 1.3 \times 1.724$$

Where:

B: volume in ml of ferrous ammonium sulfate needed for blank titration,

S: volume in ml of ferrous ammonium sulfate needed for sample titration,

W: weight in grams of sample, 0.5 is the Morality of ferrous ammonium sulfate, 0.003 is grams of organic carbon, 1.3 is walkley correction factor and 1.724 is von Bemmlen factor.

2.3.5. Soil texture analysis

Soil texture was determined using the hydrometer method (Barauah and Bathakur, 1997). A 50 g of oven- dry soil was taken and treated with 60 ml of 6 % H_2O_2 in order to remove the organic matter, and then it was heated over water bath at 80-90 ^{o} C. The previous process was repeated until frothing disappears. The residual content was transferred to a 800 ml beaker and diluted with a 400 ml distilled water, then a 100 ml of Calgon Reagent (5 % of sodium hexametaphosphate) was added, the suspension was stirred using a magnetic stirrer for 15-20 min, then it was transferred into a settling cylinder (1L) which was sealed with para - film and shaken for a 1 min. Then the hydrometer was inserted immediately into a settling cylinder and after 4 min, hydrometer reading (a) and suspension temperature were recorded. Finally, reading of hydrometer (b) after 2 hours and the suspension temperature were recorded.

The hydrometer readings were corrected according to its calibration temperature . The particle size distributions was determined as follows:

$$Silt \% = (a-b) /c \times 100$$

$$Clay \% = (b/c) \times 100$$

$$Sand \% = 100- (Silt \% + Clay \%)$$

Where:

a: the corrected hydrometer reading after 4 min

b: the corrected hydrometer reading after 2 hours

c: is the weight in grams of oven – dry sediment sample after subtraction of the weight of the oxidized organic matter.

2.4. Sample preparation

2.4.1 Total Heavy Metals Digestion

The certified reference material (CRM) (BCR - 141) was digested using an Anton Parr microwave digestion system model Multiwave 3000 (Anton Parr®, Österreich). An accurately 0.3 g of ground soil sample was transferred to pre-cleaned Prefluoroalkoxy (PFA) Teflon vessels and then a suitable amount of acids mixture were added according to the optimization procedure of the microwave digestion, Table 2.1.

The digestion PFA Teflon vessels were capped and placed inside rotor body, sealed, tightened and submitted to microwave digestion programs. Each series of digestion cycle included a sample blank which was a pre – cleaned Teflon vessel containing the same type and amount of the reagents but without the soil sample. Several digestion procedures were tried to achieve complete sample matrix decomposition, clear solutions and the best recovery rate. After microwave digestion, the digested samples were quantitively transferred to polypropylene bottle and diluted to a final volume of 50 mL. They were kept in the refrigerator until analysis.

2.4.2. Microwave Digestion:

The results of the recovery rate showed that procedure (A) that consisted of HNO_3 (7 ml), H_2O_2 (2 ml), and HF (4ml) gave the best recovery rates, Table 2.1 and it was used to digest soil samples. After digestion, the solution was clear and transferred quantitatively to a 50 mL volumetric flask by adding deionized water. Then, filtered through Whatman No. 42 filter paper and < 0.45 μm Millipore filter paper.

Table (2.1)
Microwave program of four digestion methods using the CRM (BCR- 141) soil sample

Procedure Method	Sample size (g)	Reagent (mL)	Ramping Time (min)	Temp.^{o}C	Pressure Bar	Power (watt)
A	0.3	HNO_3 7 mL H_2O_2 2mL HF 4 ml	5	180	27.6	600
B	0.3	HNO_3 6 mL HCl 2mL HF 4 mL	5	180	27.6	600
C	0.3	HNO_3 7 mL HCl 3mL	5	180	27.6	600
D	0.3	HNO_3 7 mL HF 3mL	5	180	27.6	600

2.5. Method development and optimization

2.5.1 Method validation

Several digestion procedures were performed to achieve a complete soil sample decomposition in order to obtain clear solutions and the best recovery rate. The certified reference materials (CRM) (BCR- 141r) of calcareous loam soil purchased from Institute for Reference Materials and Measurements (IRMM, Belgium) was used for analytical method validation. The BCR-141r material was digested using Anton Parr microwave digestion unit in four different acid mixtures, the digestion methods are summarized in Table 2.1. The recovery rates of analyzed trace metals were determined for each acid mixture, where the results of the recovery rate showed that procedure A gave the best recovery rate. Further, the acid mixture method A which consisted of HNO_3 (7 ml), H_2O_2 (2 ml), and HF (4ml) was used to digest soil, reference and blank samples , Table (2.2).

2.5.2. Quality control

A quality control protocol including reagent blanks, replicate samples, and certified reference material (CRM) were used to assess the precision and the accuracy of the analytical procedure. Blank samples were prepared in a similar manner to that of soil samples and were analyzed with each batch of measurements.

All analyses were made with replicate samples (n=4) for quality control assessment and the average results were reported. An external calibration method was used to build up calibration curves for each element using different concentration levels and the calibration curve was

accepted according to USEPA which exceeded ($r^2 > 0.994$) Figure (2.2)(Ming and Lean, 1998).

Table (2.2)

Analysis of heavy metals (mg/kg) of CRM soil (BCR- 141), recovery rate, LOD and LOQ (n=4).

Element	Mean	Measured Value	Recovery %	±SD	RSD	LOD*	LOQ**
Zn	283	321.82	113.60	0.69	0.21	0.015	0.044
Ni	104	113.30	108.90	0.57	0.50	0.015	0.045
Cu	45.24	41.93	92.68	0.57	1.35	0.073	0.220
Co	10.50	9.35	82.57	0.37	4.26	0.012	0.038
Fe	-	-	-	-	-	0.180	0.570
Pb	57.20	53.80	94.23	1.31	2.43	0.020	0.056

*According to digestion and analysis LOD=3.3(s/S) and LOQ =10(s/S) determined for blank (n=4).
**Method for each element using the element calibration curves.

2.5.2.1. Limit of detection (LOD)

The limit of detection (LOD) is the smallest concentration or amount of an analyte that can be reliably shown to be present or measured under defined conditions (Christian, 2004). The LOD for any analytical procedure, the point at which analysis is just feasible, may be determined by a statistical method based on measuring replicate blank samples. The limit of detection is the lowest concentration level that can be determined to be statistically different from an analyte blank. There are numerous ways that detection limits have been defined, LOD was calculated according to the following formula:

LOD= 3.3 (s/S)

Where:

s: standard deviation for blank sample

S: the slope or sensitivity of the calibration curve for the heavy metals.

2.5.2.2. Limit of Quantitation (LOQ)

The limit of quantitation (LOQ) or concentration at which quantative results can be reported with a high degree of confidence (Christian, 2004), may likewise be determined by a statistical method according to the following formula:

LOQ= 10 (s/S)

Where:

s: standard deviation for blank sample.

S: the slope or sensitivity of the calibration curve for the heavy metals.

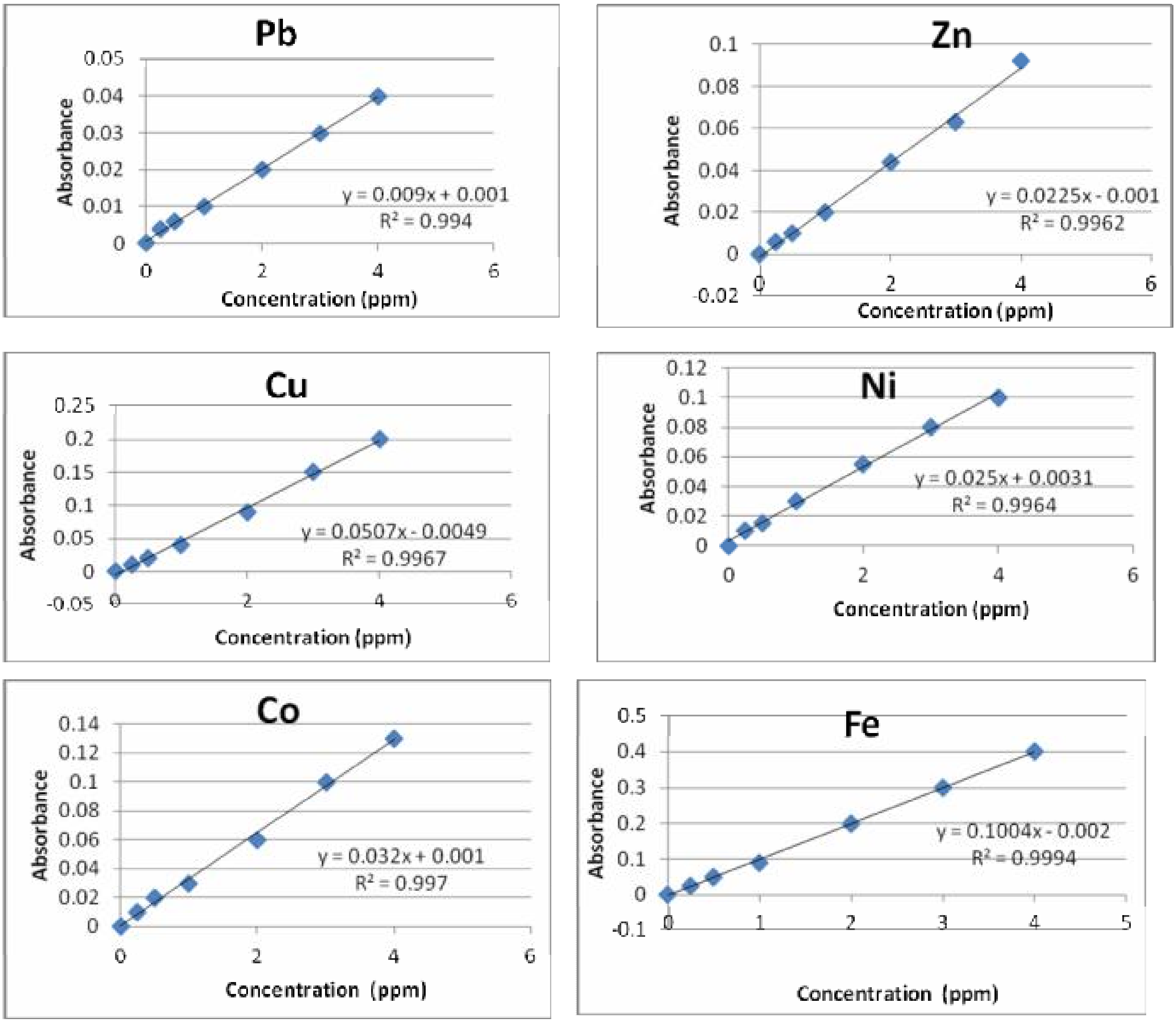


Figure (2.2)
Calibration curves for trace heavy metals

The presence of a substance may still be detected qualitatively but not quantitively with sufficient degree of reliability. In this case, the presence of a substance that cannot be detected with sufficient reliability, the content was designated as below the detection limit (<DL), and the substance was considered as non detectable (ND).

2.6 Chemical and Instrumentation

2.6.1. Glassware

All glassware and polyethylene bottles were initially cleaned with soap, washed thoroughly with tap water, distilled water and soaked in 1 % HNO_3 (v/v) for overnight to remove any pollution by heavy metals.

2.6.2. Chemicals and materials

Chemicals and materials were used for sample preparation, digestion, quantification of heavy metals, clean up, titration, and other analytical procedures were of analytical grade, and All reagents used in digestion and quantification procedures were analytical grade.

2.6.3 Instrumentation

2.6.3.1 Microwave digestion system

The certified reference material and soil samples were digested using a microwave digestion system model Multiwave 3000 (Anton parr®, Österriech). The samples were digested using 100-mL perfluoroalkoxy (PFA®) Teflon vessels (MF 100) and 16-position Rotor. The conditions for the microwave digestion system were summarized in Table 2.1.

2.6.3.2 Atomic Absorption Spectrometer (AAS)

Heavy metals concentrations were measured using an atomic absorption spectrometer (AAS) model Thermo S-Series (Thermo Scientific®, USA). The AAS was equipped with a hollow cathode lamp and a 10 cm long slot-burner head and air/acetylene flame. The operating conditions adjusted in the spectrometer were carried out according to the standard guidelines of the manufacture (Cook Book, Thermo Scientific®, USA). The hollow cathode lamp and emission wavelength, slit width, the correct coefficient for the calibration straight line, the working linear range and detection limit found for each metal were used according to the AAS cook book. The conditions of Atomic Absorption Spectrometer are presented in Table 2.3.

Table (2.3)

Standard conditions for metals using atomic absorption spectrometer

Element	Wavelength (nm)	Slit width (nm)	Fuel flow (L/min)	Lamp current (mA)	Flame description
Zn	213.8	1	1	3	Air-Acetylene
Ni	232.0	0.15	1	10	Air-Acetylene
Pb	217.0	1	1	5	Air-Acetylene
Cu	324.7	1	1	5	Air-Acetylene
Co	240.0	0.3	1	8	Air-Acetylene
Fe	248.3	1	1	12	Air-Acetylene

2.6.3.3. pH and EC meters

The pH was analyzed using a glass electrode pH–meter model HI 254 (ORP Meter®, Germany). The pH meter was calibrated using calibration buffer solutions of pH 4, pH 7, and pH 9 at 25^{o}C according to standard method (Andrew et. al., 2005). In addition EC was measured by conductivity meter model LF 750 (WTW®, Weilheim, Germany). The EC

meter was calibrated using a 0.01 *M* KCl solution at 25°C according to standard method (Andrew et. al. 2005).

2.6.3.4. Geographic Information System (GIS)

The coordination (longitudes and latitude) of the study area were cited using the geographical information system (GIS) apparatus model (GPS II plus®, USA). The coordinations were reported during the sampling activity at each sampling site and allocated on the location map, Figure 2.1.

2.6.3.5. Other equipments

Other laboratory equipments were used such as an Oven (memmert 824, Schwabach®, type 450, Germany), a magnetic stirrer (model HP-3000, Lab Companion - jeotech®, Korea), mechanical sieves (Test Sieve, 5657, HAAN®, Germany), and an high precision analytical balance with five decimal (AND-HR-202®, Japan).

Chapter Three
Results and Discussion

3.1. Physical and chemical soil properties

The physical and chemical soil properties including pH, EC, Total Organic Carbon (TOC), Calcium Carbonate Content ($CaCO_3$%), and soil texture were determined for all collected soil samples from Tafila solid waste disposal and remote control sites. The soil samples were taken from various depths of 0-20, 20-40, and 40-60 cm as illustrated in Table 3.1, Figures 3-1, 3-2, and 3-3. The heavy metal levels were determined in the investigated area to evaluate the pollution load and its potential impact on the elemental distribution pattern.

3.1.1. pH

The pH results showed that most of collected soil samples were moderately basic, Figure 3.1. The pH values were ranged from 7.68 to 8.82 in soil samples at a depth of 0-20 cm, from 7.48 to 8.68 at a depth of 20-40 cm, and from 7.33 to 8.68 at a depth of 40-60 cm. While, for the control samples, the pH values ranged from 7.12 to 8.33 at a depth of 0-20 cm, 7.1 to 7.90 at a depth of 20-40 cm, and 7.08 to 7.8 at a depth of 40-60 cm. The minimum pH value at depth 0-20 cm was found at site 21 (7.68), and the maximum pH value at the same depth was found at site 10 (8.82), the minimum pH value at depth 20-40 cm was found at site 21 (7.48), and the maximum at site 23 (8.68), and the minimum pH value at depth 40-60 cm was found at site 21 (7.33), and the maximum at sites 3 and 4 (8.68).

It was noticed that pH value of the soil samples decreased slightly with increasing the depths. Also pH of soil samples was very critical for most metals because the mobility of metals decreases with increasing pH due to formation of insoluble hydroxide, carbonate, and organic complexes (Yu et al. 1997). The high pH values for soil samples were attributed to high percent of carbonate content (Lasat, 2000; Murrary et al. 2000). The calcareous soils lead to increase pH value above 7.0, because of calcium carbonate buffering system because it increases the pH value leading to precipitate the heavy metals and limiting their mobility. In the current study, the average carbonate content was found 32%, which might explain the basic soil characteristics in the investigated area. Further, the findings of this study were compared with similar studies at other investigated sites in Jordan and the results found similar with Tarawneh study in determination of trace metals concentrations in soil of new Karak solid waste disposal site, where pH values ranged from 7.86-8.97 at 0-20 cm (Tarawneh, 2012).

Table (3.1)
Physical and chemical parameters

Sample	Depth	pH	EC*	TOC %	Sample	Depth	pH	EC*	TOC%
1	0-20	8.49	2.81	3.19		20-40	8.46	7.04	3.50
2(w1)	0-20	8.59	3.19	3.62		40-60	8.33	3.70	3.30
	20-40	7.93	1.98	3.80	21(S4)	0-20	7.68	3.44	4.30
	40-60	8.06	1.54	3.68		20-40	7.48	3.40	3.80
3(w2)	0-20	8.20	3.40	3.86		40-60	7.33	3.62	3.70
	20-40	8.27	5.80	3.56	22(S5)	0-20	8.00	3.43	4.21
	40-60	8.68	4.40	3.68		20-40	8.51	3.51	4.11
4(w3)	0-20	8.20	2.90	3.62		40-60	8.19	2.06	3.70
	20-40	8.15	2.80	3.50	23(S6)	0-20	8.53	4.12	3.22
	40-60	8.68	1.52	3.68		20-40	8.68	2.80	3.18
5(w4)	0-20	8.50	5.38	3.54		40-60	8.08	2.67	3.9
	20-40	8.59	5.48	3.72	24(S7)	0-20	8.63	1.83	4.32
	40-60	8.53	3.10	3.62		20-40	8.54	2.33	4.20
6(w5)	0-20	8.19	1.94	3.56		40-60	8.37	3.72	3.79
	20-40	8.08	2.20	3.68	25(S8)	0-20	8.18	10.20	3.68
	40-60	8.49	2.40	3.80		20-40	8.09	12.90	3.51
7	0-20	8.06	2.19	3.17		40-60	7.98	13.00	3.42
8	0-20	8.75	18.90	2.88	26(S9)	0-20	8.11	6.40	3.81
9	0-20	8.05	2.68	2.08		20-40	8.39	2.76	3.53
10	0-20	8.82	7.60	0.69		40-60	8.06	4.65	3.10
11	0-20	8.22	3.76	3.03	27(S10)	0-20	8.15	2.71	4.50
12	0-20	8.48	4.14	2.43		20-40	8.08	4.56	4.30
13	0-20	8.68	7.19	2.70		40-60	8.01	6.31	3.80
14	0-20	8.43	1.50	1.72	28	0-20	8.51	2.90	2.90
15	0-20	8.27	3.55	2.76	29	0-20	8.79	1.66	1.98
16	0-20	8.02	12.08	3.45	30(S11)	0-20	8.56	1.81	3.78
17	0-20	8.10	3.63	1.67		20-40	8.41	2.12	3.51
18(S1)	0-20	8.33	2.41	3.80		40-60	8.29	3.17	3.42
	20-40	8.27	2.48	3.61	31	0-20	8.32	1.80	2.72
	40-60	7.79	1.70	3.56	32	0-20	8.60	1.80	2.45
19(S2)	0-20	7.97	2.41	4.10	33	0-20	8.44	13.9	2.02
	20-40	8.27	2.48	3.78	34	0-20	8.08	2.23	2.55
	40-60	7.79	1.72	4.30	35(S12)	0-20	8.49	2.30	4.13
20(S3)	0-20	8.24	8.70	4.60		20-40	8.19	3.41	3.71

Continue Table (3.1)

Sample	Depth	pH	EC*	TOC%	Sample	Depth	pH	EC*	TOC%
	40-60	8.02	3.62	3.53	46	0-20	8.45	1.90	2.35
36	0-20	8.44	13.9	1.32	47	0-20	8.11	2.57	2.67
37	0-20	8.18	2.10	1.51	48	0-20	8.06	13.20	0.95
38	0-20	8.76	1.19	2.30	49	0-20	8.39	2.77	2.15
39	0-20	8.68	5.24	2.02	50	0-20	7.99	6.31	2.33
40(S13)	0-20	8.14	10.00	3.64	51	0-20	8.55	12.29	1.82
	20-40	8.01	10.20	3.10	control 1	0-20	7.58	2.50	0.73
	40-60	7.97	10.30	2.56		20-40	7.42	3.04	0.93
41	0-20	8.71	2.19	1.65		40-60	7.33	2.73	1.12
42	0-20	8.39	12.80	1.93	control 2	0-20	8.33	2.70	0.77
43(S14)	0-20	8.38	7.70	3.30		20-40	7.90	8.02	0.92
	20-40	8.21	6.90	2.90		40-60	7.80	2.95	1.01
	40-60	8.11	6.20	2.40	control 3	0-20	7.12	2.50	0.95
44	0-20	8.17	2.60	2.10		20-40	7.10	8.10	1.02
45(S15)	0-20	8.21	1.75	3.9		40-60	7.08	2.76	1.08
	20-40	7.94	2.33	2.80					
	40-60	7.68	2.49	2.51					

*mS/cm

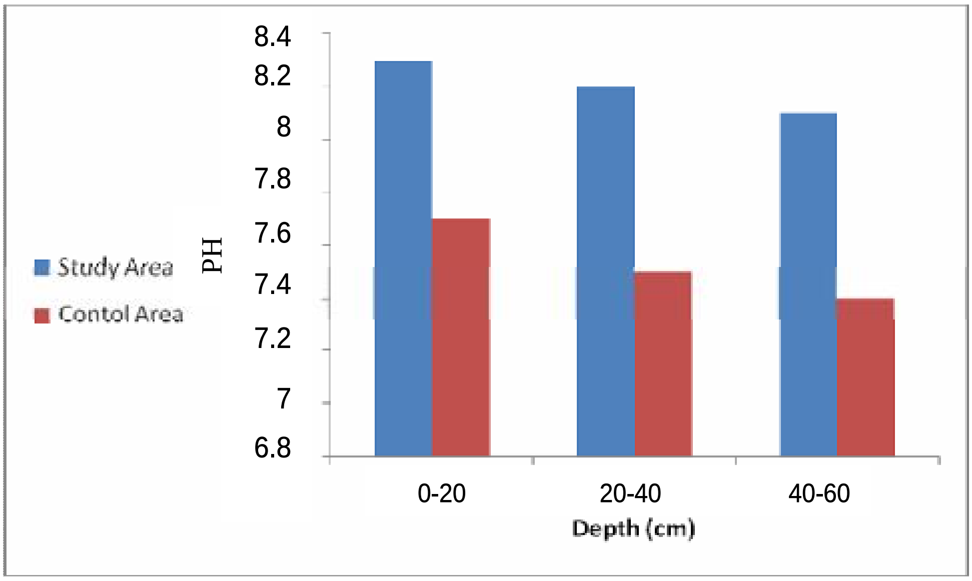


Figure (3.1)
Average pH values for study area and control area at depth (0-20, 20-40, 40-60 cm).

3.1.2. Electrical conductivity (EC)

Electrical conductivity (EC) is a numerical expression of the inherent ability of a medium to carry an electric current. since the EC and total salt concentration of an aqueous solution are closely related, EC is commonly used as an expression of the total dissolved solids concentration

of an aqueous sample, even though it is also affected by the temperature of the sample and by the mobility, valences and relative concentrations of the individual ions comprising the solution (Rhodes et al. 1999).

Electrical conductivity (EC) measurements obtained by soil-water extract of a ratio of (1:5) according to Bashour et al. (2007). The results which compare the average EC value for investigated site with the remote control site were shown on Figure 3.2. The EC values for the investigated soil samples ranged from 1.19 to 18.9 mS/cm in soil samples at a depth of 0-20 cm, 1.98 to 12.9 mS/cm at a depth of 20-40 cm, and 1.52 to 13.0 mS/cm at a depth of 40-60 cm. However, the remote control sites showed lower EC values which ranged from 2.5 to 2.7 mS/cm at a depth of 0-20 cm, 3.04 to 8.1 at a depth of 20-40 cm, and 2.73 to 2.95 mS/ cm at a depth of 40-60 cm. The minimum EC value at depth 0-20 cm found at site 38 (1.19 mS/cm), and the maximum EC value at depth 0-20 cm at site 8 (18.9 mS/cm). However, the minimum EC value at depth 20-40 cm found at site 2 (1.98 mS/cm), and the maximum EC value at depth 20-40 cm at site 25 (12.9 mS/cm). Finally, the minimum EC value at depth 40-60 cm found at site 4 (1.52 mS/cm) and the maximum EC value at depth 40-60 cm at site 25 (13 mS/cm), Tables 3.2 and 3.3.

By comparing the EC values between study and control areas, it was showed significant differences that might be due to the impacts of solid waste disposal activities that taken place in investigated area. These results were in agreement with findings found by Jaradat et al. (2005) and Al Momani (2003), where they found that the increase in total dissolved solids as the sun evaporating water from soils and leaving the salts in soils, then, natural processes carry salts from surface to downward. Furthermore, the findings of this study compared with similar study at other investigated sites in Jordan. For example, the results were similar to the findings of Tarawneh (2012) for determination of trace metals concentrations in soil samples collected from the new Karak solid waste disposal site, where EC ranged from 1.3-24.6 mS/cm at 0-20 cm (Tarawneh, 2012).

Table (3.2)
Mean, maximum, minimum, SD and median of EC (mS/cm) values at three depths for soil samples

Depths	Mean	Maximum	Minimum	±SD	Median
0-20	5.06	18.90	1.19	4.06	2.90
20-40	4.40	12.90	1.98	3.11	3.10
40-60	4.20	13.00	1.52	2.98	3.45

Table (3.3)
Mean, maximum, minimum ,median, and SD of EC (mS/cm) values at three depths for control samples

Depths	Mean	Maximum	Minimum	±SD	Median
0-20	2.60	2.70	2.50	0.11	2.50
20-40	3.60	8.10	3.04	0.53	3.51
40-60	2.80	2.95	2.73	0.11	2.76

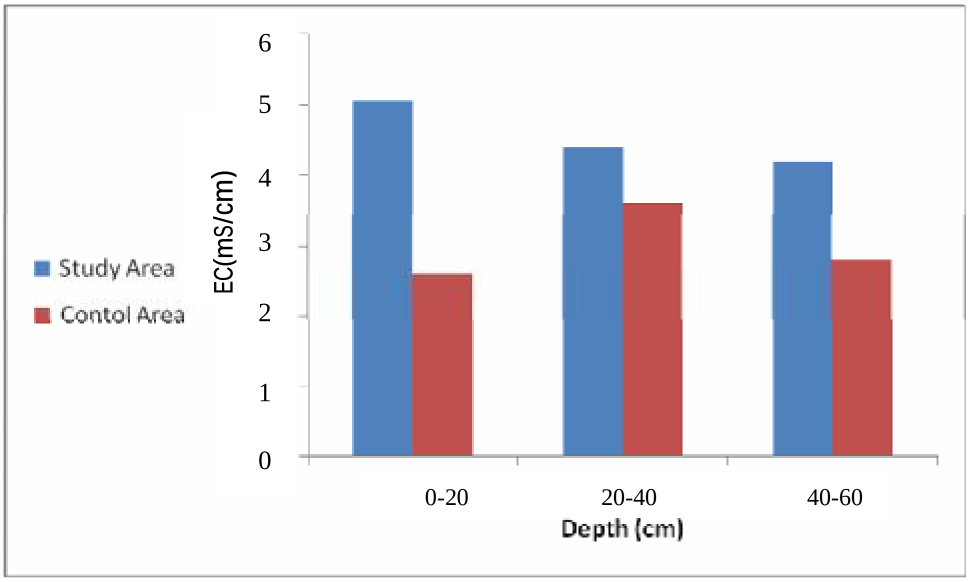


Figure (3.2)
Comparison of average EC (ms/cm) values for study and control area at depth (0-20, 20-40, 40-60 cm)

3.1.3. Total Organic Carbon (TOC %)

Soils contain a large variety of organic materials ranging from simple sugars and carbohydrates to more complex proteins, fats, waxes, and organic humic and fulvic acids.

Total organic carbon is a measure of which one of the chemical components of organic matter that is often used as indicators of its presence in a soil, also naturally occurring organic carbon forms are derived from the decomposition of plants and animal and that are derived as a result of pollution through anthropogenic activities, and due to nature of rocks in the study area .

The percentage of TOC % of soils differs between different sites and depths, the result showed that the TOC% in investigated soil samples ranged from 0.69 to 4.60 in soil samples at a depth of 0-20 cm, 2.8 to 4.3 at a depth of 20-40 cm, and 2.4 to 4.3 at a depth of 40-60 cm, Tables 3.4 and 3.5. While, lower amounts of TOC was determined for the remote control area that ranged from 0.73 to 0.95 % at a depth of 0-20 cm, 0.92 to 1.02 % at a depth of 20-40 cm, and 1.01 to 1.12 % at a depth of 40-60 cm. The minimum TOC% value at depth 0-20 cm found at site 10 (0.69%), and the

maximum TOC% value at depth 0-20cm at site 20 (4.6%), the minimum TOC% value at depth 20-40cm found at site 22 (4.11%), and the maximum TOC% value at depth 20-40cm was found at site 45 (2.8%), and the minimum TOC% value at depth 40-60cm found at site 43 (2.4%), and the maximum TOC% value at depth 40-60cm was found at site 19 (4.3), Figure 3.3.

The significant differences in TOC% values between study and control area can be attributed to the organic waste disposal at the investigated area including food residues, animal residue, cartons, paper, oils, textures, wood fibers, leather scraps, pulp mill waste, wastewater and sludge of biological waste. The total organic carbon at top soil profile found relatively high due to above recent mentioned anthropogenic activities in addition to rainfall and snowfall during winter season that might facilitate organic matter solubility. These values were exceeding the normal range of soil organic matter in Jordan which ranged from 0.9 to 1.7 (Ministry of Agriculture, 2012). Further, the findings of this study were compared with similar study at other investigated site in Jordan and the results were dissimilar such as the study of heavy metals pollution of air and soil in Karak solid waste disposal site, as the total organic matter was found at a higher levels in this study than others (Jiries et al. 1996). Additionally, the TOC ranged over 0.91-3.26 % at 0-20 cm at new Karak solid waste disposal site (Tarawneh, 2012).

Table (3.4)

Mean , maximum, minimum, SD, and median of TOC % values at three depths for soil samples

Depths	Mean	Maximum	Minimum	±SD	Median
0-20	2.88	4.60	0.69	0.98	2.90
20-40	3.65	4.30	2.80	0.35	3.61
40-60	3.48	4.30	2.40	0.47	3.62

Table (3.5)

Mean, maximum, Minimum, SD and, median of TOC % values at three depths for control samples

Depths	Mean	Maximum	Minimum	±SD	Median
0-20	0.82	0.95	0.73	0.11	0.77
20-40	0.96	1.02	0.92	0.05	0.93
40-60	1.07	1.12	1.01	0.05	1.08

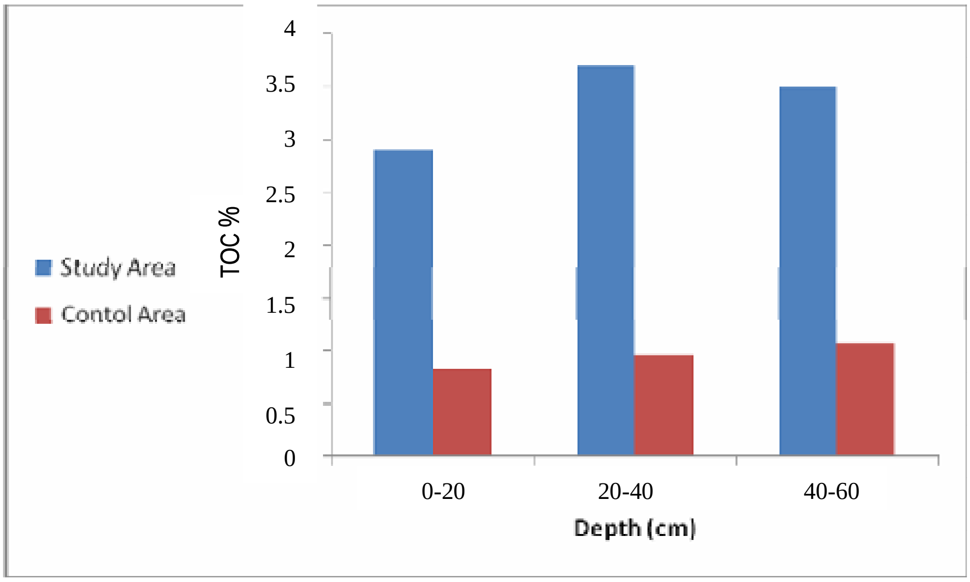


Figure (3.3)
Average TOC % values for study area and control area at depth (0-20, 20-40, 40-60 cm)

3.1.4. Calcium Carbonate Content ($CaCO_3$%)

Calcium carbonate is a major component of calcareous soils, ranges from a few percent in slightly calcareous soils to more than 80 percent in some extremely calcareous soils and its distribution down the soil profile affecting soil physical and chemical characteristics (Bashour et al. 2007). Also soil retention of metals such as Zn and Cu was directly related to carbonate soil content between the clay and silt fractions. When total $CaCO_3$ % was less than 20 %, the retention of those elements was affected mainly by the total amount of carbonates, but when it was above 20 %, nature of carbonates was more important in governing retention.

The percent of $CaCO_3$% was determined for 30 samples and the result showed that the $CaCO_3$% highly varied in the investigated soil samples which ranged over 21.3 - 74.5% with an average value of 31.51 %, Table 3.6. This finding was located within the normal average value of carbonate percent in calcareous Jordanian soils.

Table (3.6)
Calcium Carbonate Content $CaCO_3$%

Samples	Depth (cm)	$CaCO_3$%
18(S1)	0-20	74.50
	20-40	61.50
	40-60	61.00
20(S3)	0-20	47.00
	20-40	50.50
	40-60	48.00
24(S7)	0-20	35.18
	20-40	50.10
	40-60	47.75
2(W1)	0-20	30.50
	20-40	26.99
	40-60	42.50
3(W2)	0-20	47.00
	20-40	33.00
	40-60	21.30
4(W3)	0-20	23.51
	20-40	35.50
	40-60	34.52
1	0-20	47.50
7	0-20	53.50
10	0-20	44.50
13	0-20	48.50
15	0-20	44.00
21	0-20	32.00
28	0-20	35.00
38	0-20	27.50
41	0-20	27.22
42	0-20	40.00
44	0-20	22.90
50	0-20	26.67

3.1.5 Correlation Coefficients between soil parameters

The correlation coefficients between all analyzed parameters (pH, EC, and TOC%) , were calculated in order to evaluate the relationship between the soil physical and chemical parameters at different soil depths, Tables 3.7, 3.8 and 3.9. It was found at 0-20 cm depth there were no significant correlation between pH and EC (r^2 = 0.125), a weak inverse correlation between TOC and EC value (r^2 = -0.116) followed by pH and TOC % (-0.023). Further, at 20-40 cm depth there were weak inverse correlation between pH and EC (r^2 = -0.201) and TOC and EC value (r^2 = -

0.305), while significant correlation was found between pH and TOC % (r^2 = 0.637). Finally, at 40-60 cm depth there were no significant correlation neither between pH and EC nor between TOC and EC. While, significant correlation was found between pH and TOC % (0.584). In General, these results showed that the pH, EC, and TOC% values were independent on each other for most of the investigated sample, although significant correlation was found between pH and TOC for some samples.

Table (3.7)

Correlation matrices between soil parameters at depth (0-20)

	pH	EC(mS/cm)	TOC%
pH	1.00		
EC	0.125	1.00	
TOC%	-0.023	-0.116	1.00

Table (3.8)

Correlation matrices between soil parameters at depth (20-40 cm)

	pH	EC(mS/cm)	TOC%
pH	1.00		
EC	-0.201	1.00	
TOC%	0.637	-0.305	1.00

Table (3.9)

Correlation matrices between soil parameters at depth (40-60 cm)

	pH	EC(mS/cm)	TOC%
PH	1.00		
EC	0.005	1.00	
TOC%	0.584	-0.053	1.00

3.2 Soil texture

The soil texture is the result of the physical and chemical breakdown of rocks and minerals which known as weathering (Cauley et al. 2005).

Soil texture was determined for 13 soil samples namely: 1, 4, 8, 12, 16, 20, 24, 28, 32, 36, 40, 44, and 50 using the hydrometer method. The result is presented in Table 3.10. The soil in the study area can be classified as loamy soil according to the standard US Department of Agriculture (USDA) soil texture classification triangle, Table 3.10. Loamy soil is a material that is medium-textured. It feels as though it contains a relatively even mixture of sand, silt, and clay because clay particles, with their small size, high surface areas, and high physical and chemical activities, greater influence on soil properties, loam tends to be rather soft and friable (Brown, 1998).

loamy soils are good infiltration of water. The transport mechanics of heavy metals through loamy soils has great interest because of possibility of groundwater pollution through metal leaching.

Table (3.10)

Soil Texture for selected samples for the investigated area.

Samples	Depth (cm)	Silt %	Sand %	Clay %	Texture
1	0-20	31.5	49.0	19.5	Loamy
	0-20	30.0	49.0	21.0	Loamy
4 (w3)	20-40	30.5	48.5	21.0	Loamy
	40-60	32.0	49.0	19.0	Loamy
8	0-20	29.5	48.5	22.0	Loamy
12	0-20	30.5	49.0	20.5	Loamy
16	0-20	30.5	48.5	21.0	Loamy
	0-20	31.5	48.5	20.0	Loamy
20 (S3)	20-40	30.5	49.0	20.5	Loamy
	40-60	31.0	49.0	20.0	Loamy
	0-20	31.5	48.5	20.0	Loamy
24(S7)	20-40	31.0	49.0	20.0	Loamy
	40-60	31.0	48.5	20.5	Loamy
28	0-20	31.0	48.5	20.5	Loamy
32	0-20	31.5	49.0	19.5	Loamy
36	0-20	32.0	48.0	20.0	Loamy
	0-20	31.0	49.0	20.0	Loamy
40(S13)	20-40	32.0	48.0	20.0	Loamy
	40-60	31.5	49.0	19.5	Loamy
44	0-20	31.5	49.0	20.0	Loamy
50	0-20	31.5	49.0	19.0	Loamy
	Average	**31.09**	**48.74**	**20.17**	**Loamy**

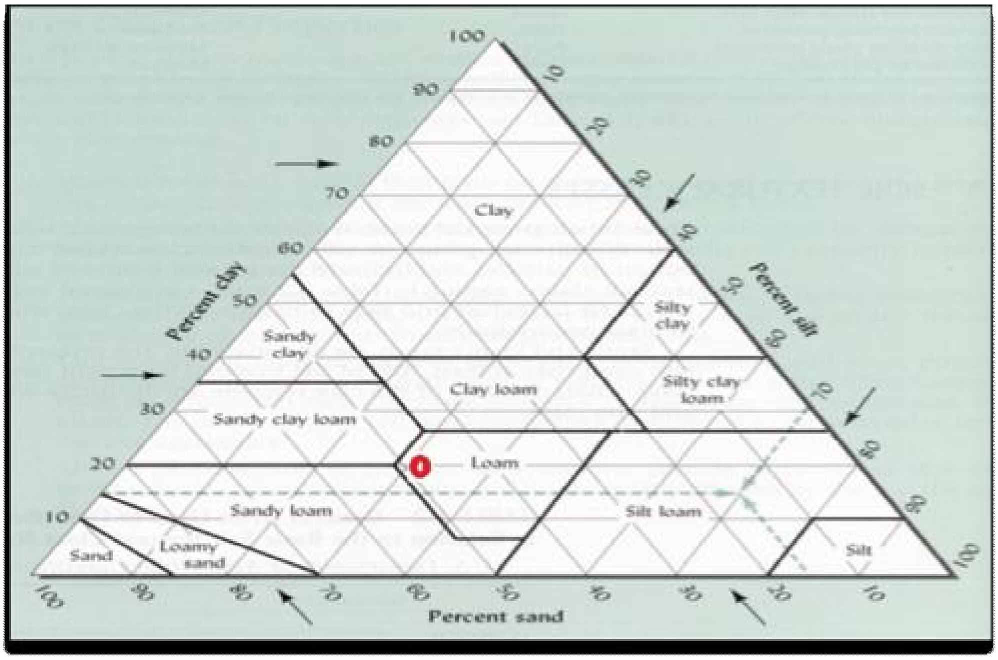


Figure (3.4)
Soil Texture triangles according to USDA.

3.3. Analytical Method Validation

The total concentrations of six metals (Zn, Ni, Pb, Cu, Co, and Fe) were analyzed quantatively based on external calibration curves for series of standard solutions using flame atomic absorption spectrometer (FAAS). The calibration curves of these elements were determined with best regression lines with correlation coefficient (r^2> 0.994), as shown in Figure (3.5). The analytical method accuracy was checked using a certified reference material (CRM) of calcareous soil number (CRM 141r) that contained known metals concentration. The certified reference material (CRM) was digested using the same analytical procedure used for soil samples and analyzed subsequently using FAAS. The results were compared with certified CRM values and the percent recovery was computed, Table 3.11. It was found that the procedure (A) which composed of a mixture of HNO_3, H_2O_2, and HF using the microwave had a robustness procedure with recovery ranged from 82.57 to 113.6% with relative standard deviation (RSD %) of less than 10%, procedure (B) 21.9 to 92 %, procedure (C) 23-92 %, and procedure (D)18.8 to 88 %, Table 2.1.

Furthermore, the limit of detection (LOD) and limit of quantitation (LOQ) were determined based on statistical formula in section 2.5.2.1 and 2.5.2.2. Which was calculated for blank samples (4 replicates) after performing the complete digestion and analysis procedure in similar manner as the soil samples (Christain, 2004). The results of validation parameters including recovery rates, standard deviation of recovery rate

and its relative standard deviation, in addition to the LOD and LOQ for all analyzed heavy metals on basis of blank samples are presented .

3.4 Heavy Metals

The heavy metal concentrations (mg kg^{-1}) in all investigated soil samples are illustrated in Table 3.11. The results showed big variations in the concentration of heavy metals among investigated sites and at different soil depths that might be due to the difference in their sources, type of solid waste disposal, and soil properties. The variation in concentrations of heavy metal with different soil depths may be due to leaching of the heavy metals through the soil profiles. The metal transport depends on physical and chemical properties of soils which may vary due to anthropogenic impact, sorption properties of soil complex which affected on pH values, they all play a very important role in giving the soil the ability to a adsorb, exchange, oxidize, reduce, catalyze, and precipitate chemicals and metal ions in particular (Dube et al. 2001).

Table (3.11)
Concentration of heavy metals (mg kg^{-1}) in soil samples of study area.

Samples	Depth (cm)	Zn	Ni	Pb	Cu	Fe	Co
1	0-20	145.45	132.65	99.45	180.00	80.00	96.23
2(w1)	0-20	195.45	141.58	101.32	160.00	118.00	51.37
	20-40	36.30	168.25	107.21	140.00	28.00	67.91
	40-60	95.45	177.58	108.21	180.00	76.00	76.53
3(w2)	0-20	100.00	137.42	131.26	140.00	93.00	59.61
	20-40	40.90	146.32	141.25	140.00	41.00	70.19
	40-60	154.54	155.64	142.09	240.00	91.00	74.09
4(w3)	0-20	95.45	128.36	129.95	120.00	86.00	62.83
	20-40	154.54	139.54	119.53	180.00	125.00	69.70
	40-60	86.36	147.68	118.42	280.00	111.00	79.68
5(w4)	0-20	127.27	152.39	151.36	160.00	127.00	58.31
	20-40	86.36	166.51	133.59	200.00	55.00	60.25
	40-60	40.90	173.72	130.51	240.00	42.00	62.81
6(w5)	0-20	54.54	158.26	149.61	100.00	129.00	63.12
	20-40	218.18	169.53	135.61	140.00	117.00	67.29
	40-60	100.00	186.33	132.67	180.00	75.00	72.94
7	0-20	136.36	116.91	198.96	120.00	69.00	90.43
8	0-20	318.18	198.62	210.34	260.00	104.00	99.50
9	0-20	36.36	109.84	198.63	220.00	75.00	102.11
10	0-20	304.54	115.69	224.30	100.00	80.00	100.92
11	0-20	336.36	95.62	202.09	80.00	76.00	88.49
12	0-20	109.09	88.66	284.67	220.00	72.00	92.15
13	0-20	31.81	111.94	241.60	220.00	40.00	78.95
14	0-20	72.72	142.36	199.28	260.00	101.00	103.73
15	0-20	122.72	119.87	278.65	280.00	95.00	99.41
16	0-20	68.18	123.54	239.81	180.00	107.00	92.81
17	0-20	86.36	133.57	63.51	60.00	104.00	99.76

Continuo table (3: 11)

18(S1)	0-20	72.22	135.61	188.53	100.00	49.00	98.11
	20-40	22.72	159.81	175.92	180.00	79.00	99.19
	40-60	27.27	171.22	170.18	280.00	63.00	100.30
19(S2)	0-20	90.90	188.35	191.67	140.00	49.00	97.23
	20-40	36.36	193.10	172.37	160.00	31.00	102.30
	40-60	40.90	233.51	168.90	240.00	77.00	109.15
20(S3)	0-20	122.72	177.01	231.09	180.00	84.00	99.10
	20-40	463.53	189.15	196.37	200.00	83.00	100.09
	40-60	154.54	255.37	193.57	260.00	52.00	113.60
21(S4)	0-20	45.45	191.25	197.69	120.00	65.00	98.36
	20-40	36.36	212.81	181.13	160.00	24.00	99.50
	40-60	100.00	261.13	177.39	180.00	103.00	110.80
22(S5)	0-20	122.72	210.35	199.07	120.00	93.00	95.42
	20-40	77.27	249.15	188.37	120.00	44.00	97.31
	40-60	40.90	253.48	161.67	160.00	94.00	101.30
23(S6)	0-20	27.27	261.31	212.39	260.00	47.00	100.20
	20-40	81.81	269.81	199.07	320.00	72.00	109.95
	40-60	109.09	283.51	129.37	300.00	90.00	109.00
24(S7)	0-20	140.90	188.94	209.37	60.00	73.00	97.41
	20-40	59.09	194.29	199.12	100.00	63.00	99.95
	40-60	31.81	271.38	183.09	160.00	51.00	99.24
25(S8)	0-20	18.18	128.67	219.17	160.00	36.00	97.61
	20-40	77.27	142.37	220.13	180.00	50.00	98.61
	40-60	36.36	191.12	222.39	220.00	66.00	100.92
26(S9)	0-20	36.36	94.61	200.91	100.00	49.00	94.09
	20-40	136.36	101.54	201.31	160.00	67.00	96.43
	40-60	131.81	129.67	200.67	140.00	82.00	97.53
27(S10)	0-20	72.72	108.96	219.89	80.00	39.00	99.05
	20-40	550.00	119.16	205.00	140.00	78.00	103.23
	40-60	127.27	139.25	196.35	260.00	75.00	105.10
28	0-20	54.54	287.65	199.73	220.00	55.00	96.38
29	0-20	136.36	187.29	77.59	280.00	103.00	102.91
30(S11)	0-20	72.72	151.11	160.36	260.00	52.00	100.15
	20-40	77.27	164.19	159.67	200.00	79.00	110.60
	40-60	100.00	180.92	155.61	380.00	105.00	110.00
31	0-20	72.72	289.92	100.49	140.00	86.00	98.12
32	0-20	190.90	138.11	65.38	220.00	78.00	97.15
33	0-20	122.72	167.91	78.16	180.00	118.00	95.22
34	0-20	127.27	125.32	81.26	180.00	92.00	93.17
35(S12)	0-20	86.36	81.65	99.51	80.00	47.00	99.50
	20-40	86.36	113.27	100.19	260.00	95.00	107.09
	40-60	54.54	111.37	99.53	360.00	39.00	110.62
36	0-20	136.36	200.39	88.11	200.00	104.00	89.69
37	0-20	109.09	219.51	128.62	180.00	52.00	91.92
38	0-20	90.90	193.55	95.65	140.00	97.00	93.66
39	0-20	327.27	173.71	82.63	60.00	80.00	97.65
40(S13)	0-20	154.54	161.22	87.52	180.00	67.00	94.16
	20-40	127.27	173.81	89.23	200.00	78.00	113.22
	40-60	40.90	181.11	88.16	200.00	70.00	114.20
41	0-20	109.09	192.31	71.92	220.00	83.00	100.05
42	0-20	81.81	179.62	77.59	220.00	90.00	99.61
43(S14)	0-20	68.18	209.11	167.34	180.00	42.00	100.40
	20-40	131.81	221.38	157.37	380.00	103.00	122.61
	40-60	109.09	267.51	161.02	180.00	64.00	111.83
44	0-20	177.27	218.34	83.51	260.00	95.00	93.51

Continuo table (3)

45(S15)	0-20	95.45	184.32	71.61	60.00	83.00	97.18
	20-40	54.54	191.21	77.08	120.00	64.00	111.68
	40-60	77.27	210.86	79.93	180.00	82.00	112.91
46	0-20	386.36	155.37	66.91	200.00	103.00	99.20
47	0-20	104.54	128.91	67.19	260.00	100.00	98.53
48	0-20	122.72	272.30	70.65	180.00	111.00	97.63
49	0-20	336.36	211.61	69.34	278.00	103.00	96.08
50	0-20	150.00	168.44	73.67	60.00	312.00	93.17
51	0-20	395.45	193.28	81.37	120.00	120.00	95.62
Control 1	0-20	31.81	72.61	93.61	20.00	125.00	23.71
	20-40	18.18	89.13	90.05	40.00	17.00	25.83
	40-60	13.53	101.14	92.16	80.00	22.00	30.94
Control 2	0-20	18.18	68.61	86.64	40.00	72.00	21.67
	20-40	13.53	97.14	93.03	30.00	13.00	26.37
	40-60	9.09	99.05	88.85	50.00	35.00	33.52
Control 3	0-20	13.53	65.41	103.63	20.00	135.00	22.10
	20-40	9.09	93.27	93.53	70.00	19.00	28.26
	40-60	13.53	99.61	94.09	90.00	31.00	32.79

3.4.1 Zinc

The concentrations of Zinc (Zn) in soil samples collected from the Tafila solid waste disposal site ranged from 18.18 to 395.45 mg kg^{-1} with an average value of 134.81 mg kg^{-1} at 0-20 depths which exceed that value for remote control site by more than 10 folds (13.53 to 31.81 mg kg^{-1} with average of 21.21 mg kg^{-1}). The highest Zn concentration found at site 51 and the lowest at site 25. The Geographic Information System Map (GIS-map) shows the distribution pattern of Zn in the investigated area, Figure 3.5. Generally, Zinc occurs naturally in soil (about 70 mg kg^{-1} in crustal rocks) (Davies et al. 1988). Zinc may come from food residues which that contain a certain concentrations of Zn, lubricating oils, tires of motor vehicles and Zinc in carburetors. Additionally, it was found that 93% of the investigated samples have levels below the range of Mc Grath et al. (2001). The typical range of trace elements in non-polluted soil is illustrated in Table 3.12, the average Zn content was found in range 10-200 mg kg^{-1} for non-polluted soil (Mc Grath et al. 2001). However, only 7% of the investigated soil samples showed concentrations higher than this average, and the GIS contour map shows the concentrations levels of Zn using the colored map Index which was given in five ranges (15-95, 96-170, 171-245, 246-320, and 321-400 mg kg^{-1}), Figure 3.5. Showed that the highest concentrations of Zn were dominated in the north-west and southern parts of the solid waste disposal site.

Table (3.12)
Typical range of trace elements in non-polluted soil (Mc Grath et al. 2001)

Element	Range (mg kg^{-1}) (Total content)
Zn	10-200
Ni	0.5-100
Pb	2.1-80
Cu	2-100
Co	1-25
Fe	------

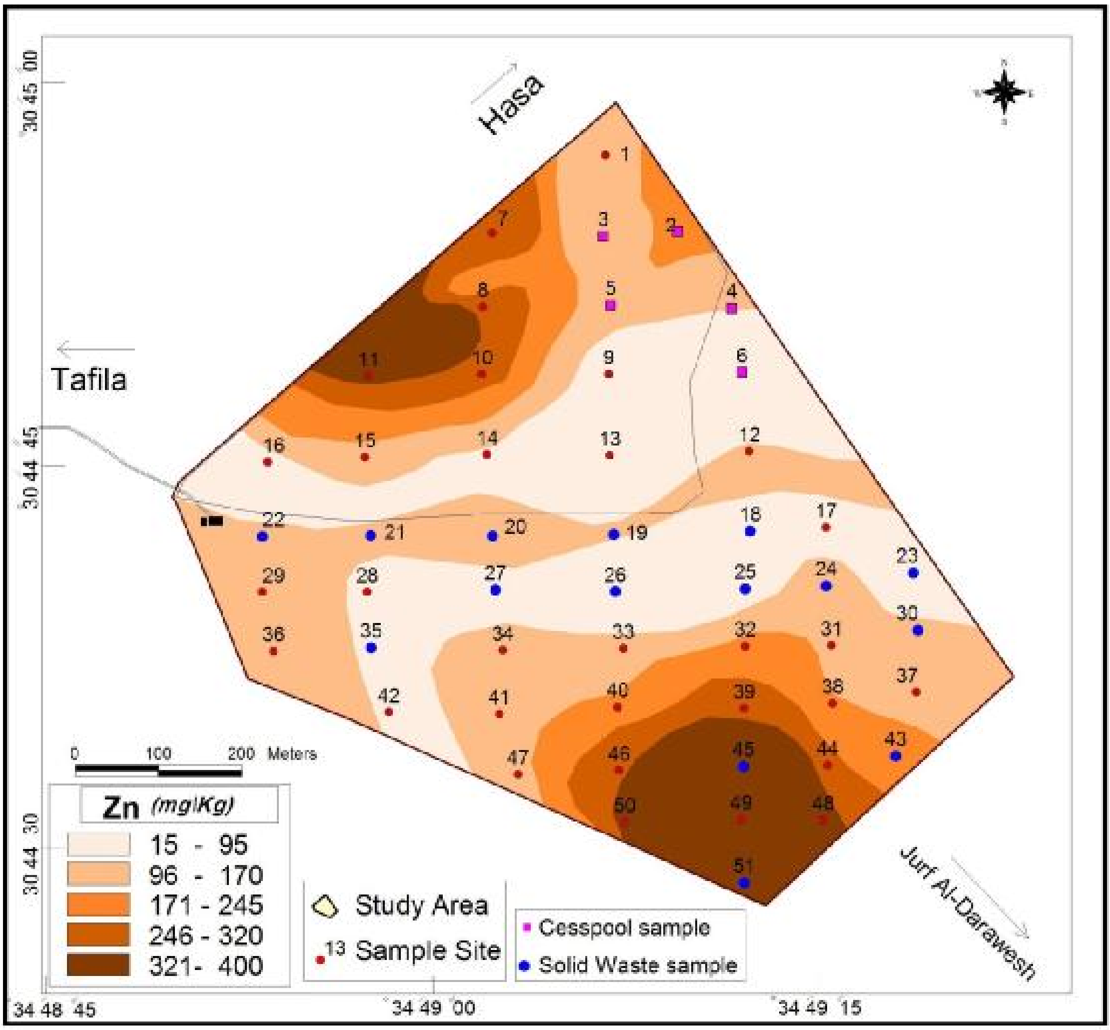


Figure (3.5)
Distribution of Zn Concentrations using GIS contour map (0-20 cm).

The concentrations of zinc in soil samples at 20-40 cm depths ranged from 23 to 550 mg kg^{-1} with an average value of 127 mg kg^{-1}, while, it was ranged from 9 to 18 mg kg^{-1} with an average of 14 mg kg^{-1} for the remote control area. The highest value of Zn was found at site 27 and the lowest value at site 21. The variation in the concentrations of Zn metal with depths is shown on Figure 3.6. Finally, the concentrations of zinc was varied between 9 and 14 mg kg^{-1} with an average of 12 mg kg^{-1} in the control area at 40-60 cm depths compared to 27 and 154 mg kg^{-1} with an average of 83 mg kg^{-1} in the study area at the same depths. The highest concentration of Zn was found at site 2 and the lowest at site 18. Figure 3.6 shows the significant variation in the concentrations of Zn metals with depths and site. It was noticed that leachability of Zn to higher soil depth has been occurred and might be due to the dominant wet weather conditions in winter and liquid waste disposal.

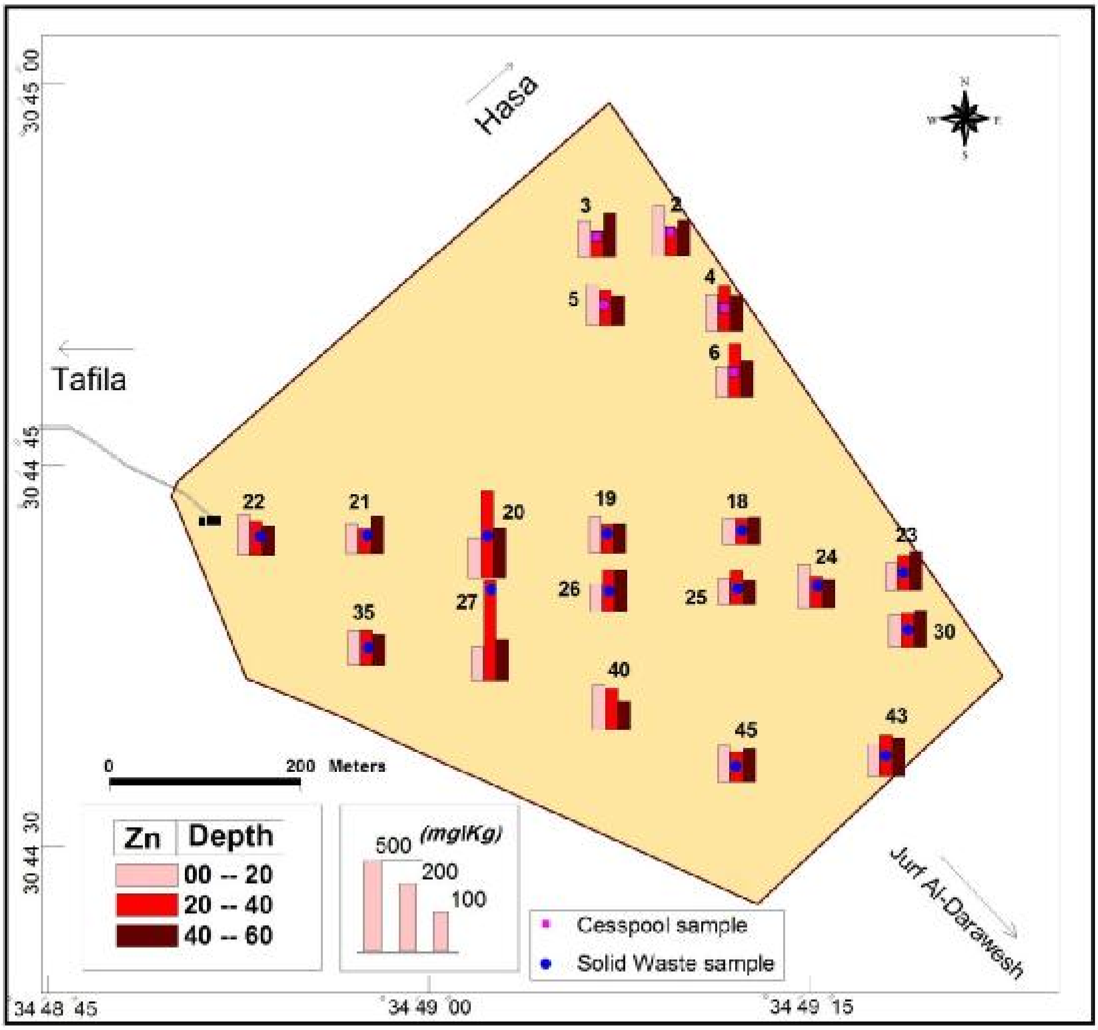


Figure (3.6)
Distribution of Zn Concentrations using GIS map at 0-20,20-40, and 40-60 cm.

3.4.2 Lead

The concentrations of Lead (Pb) in soil samples collected from the Tafila solid waste disposal site was ranged from 63.51 to 284.67 mg kg^{-1} with an average value of 145.83 mg kg^{-1} at depths 0-20 cm which exceeded that value for remote control site 86.64 to 103.63 mg kg^{-1} with average of 94.69 mg kg^{-1}. The highest Pb concentration was found at site 12 and the lowest value at site 17. The Geographic Information System Map (GIS-map) shows the distribution pattern of Pb in the investigated area, Figure 3.7. The highest Pb concentrations were located at the western and middle sites of the investigated area. Lead may come from agriculture wastes as a result of fertilizer use, sewage sludge from wastewater treatment plants, and automobile exhaust. Additionally, it was found that 14.28 % of the investigated samples were contained concentration levels below the range of Mc Grath et al. (2001). The typical range of trace heavy elements in non-polluted soil is illustrated in Table 3.12 , the average Pb content is range over 2.1 - 80 mg kg^{-1} for non-polluted soil (Mc Grath et al. 2001). While, 85.72 % of the investigated samples contained concentration levels above the range. The GIS contour map shows the concentration levels of Pb using the colored map Index which was given in five ranges (60-110, 111-150, 151-200, 201-240, and 241-283 mg kg^{-1}), Figure 3.7.

The concentrations of Lead in soil samples at 20-40 cm depths ranged from 77.08 to 220.13 mg kg^{-1} with an average value of 157.94 mg kg^{-1}, while, it was ranged from 90.05 to 93.53 mg kg^{-1} with an average of 92.9 mg kg^{-1} for the remote control area. The highest value of Pb found at site 25, and the lowest value at site 45. The variation in the concentrations of Pb with depths are shown on Figure 3.8.

Finally, the concentration of lead was varied between 88.85 and 94.09 mg kg^{-1} with an average of 91.70 mg kg^{-1} in the control area at 40-60 cm depths compared to 79.3 and 222.39 mg kg^{-1} with an average of 146.21 mg kg^{-1} in the study area at the same depth. The highest concentration of Pb was found at site 25 and the lowest at site 45. Figure 3.8 shows the significant variation in the concentrations of Pb with soil depths and site.

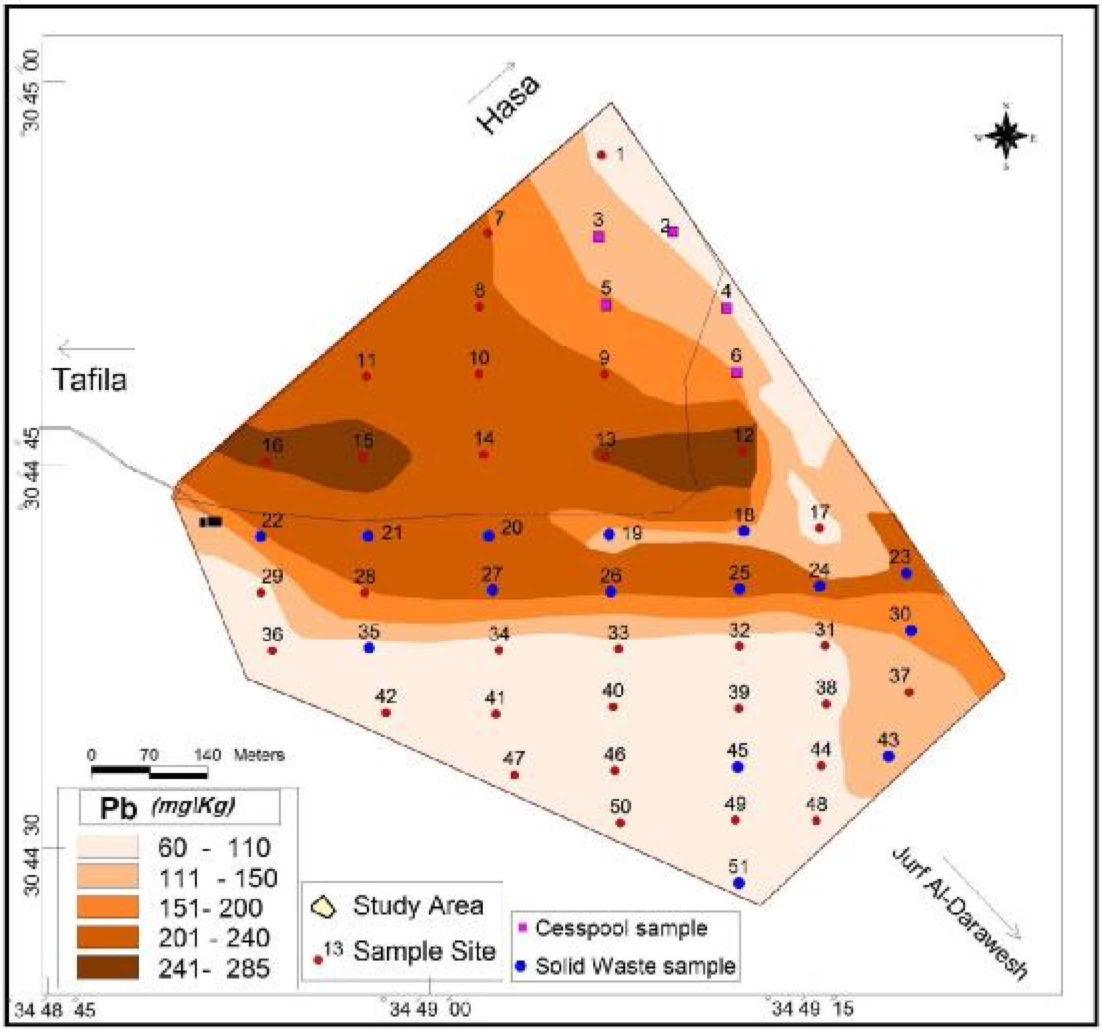


Figure (3.7)
Distribution of Pb Concentrations using GIS map
(0-20 cm).

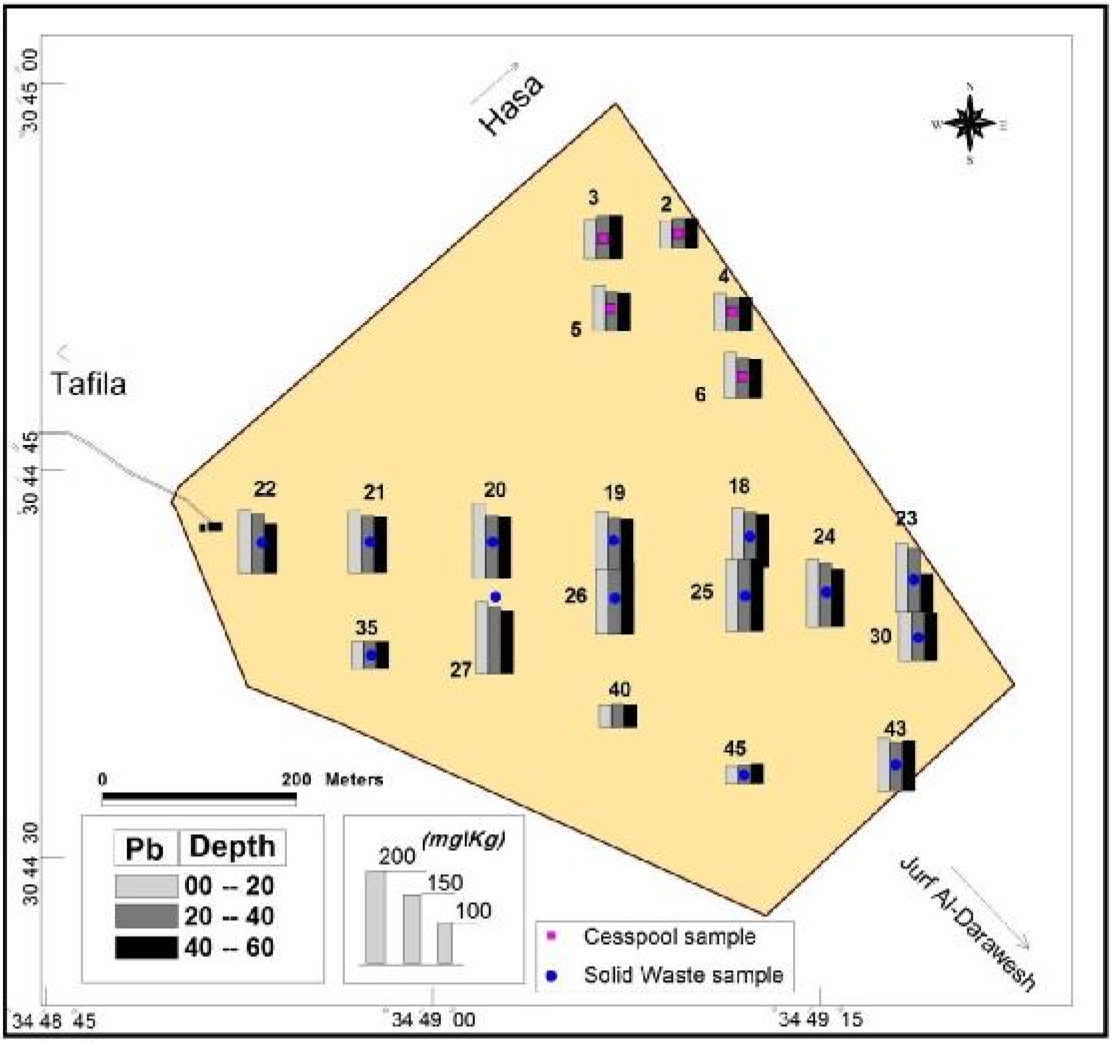


Figure (3.8)

Distribution of Pb Concentrations using GIS map at 0-20, 20-40, and 40-60 cm.

3.4.3 Cobalt

The concentration of Cobalt (Co) in soil samples collected from the Tafila solid waste disposal site ranged from 51.37 to 103.73 mg kg^{-1} with an average value of 92.88 mg kg^{-1} at a depth 0-20 cm which exceeded that value for remote control site 21.67 to 23.71 mg kg^{-1} with average of 22.52 mg kg^{-1}. The highest value of Co was found at site 14 and the lowest value of Co at site 2. The Geographic Information System Map (GIS-map) shows the distribution pattern of Co in the investigated area, Figure 3.9. It was noticed that Co was distributed on over all investigated sites in similar concentration levels except in the north-eastren part which was found at lower concentration levels. Cobalt may come from the plastic waste that is 5% of the input solid waste at the investigated disposal site (Ross, 1996).

The results showed elevated concentration levels of Co than in the control area. While, 100% of the samples contained concentration levels above the range of non-polluted soil. The GIS contour map shows the

concentration levels of Co using the colored map Index which was given in five ranges (50-65 ,66-75,76-85,86-95,and 95-105 mg kg^{-1}), Figure 3.9.

It was found that the investigated area was contaminated with elevated Co concentration compared to the remote reference area. The Co concentration ranged from 60.25 to 113.22 mg kg^{-1} with an average value of 93.88 mg kg^{-1} at 20-40 cm depth, while, it was ranged from 25.83 to 28.26 mg kg^{-1} with an average of 26.83 mg kg^{-1} for the remote control area. The highest value of Co found at site 40 and the lowest value at site 5. The variation in the concentrations of Co metal with depths is shown on Figures 3.9 and 3.10. Finally, the concentrations of Cobalt was varied between 30.94 and 33.52 mg kg^{-1} with an average of 98.63 mg kg^{-1} in the control area at 40-60 cm depths compared to 62.81 and 114.2 mg kg^{-1} with an average of 32.45 mg kg^{-1} in the study area. The highest concentration of Co was found at site 40 and the lowest at site 5. Figure 3.10 shows the significant variation in the concentrations of Co metal with soil depths and site .

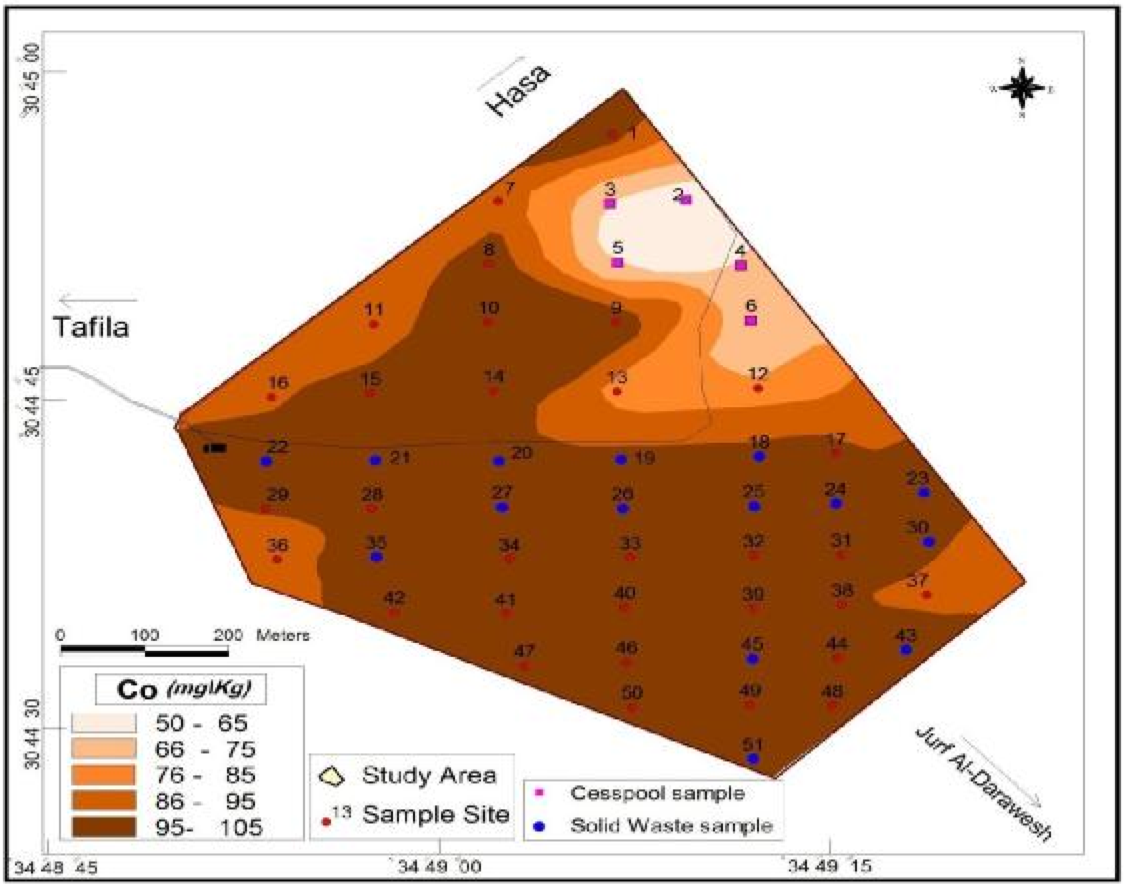


Figure (3.9)
Distribution of Co Concentrations using GIS map
(0-20 cm).

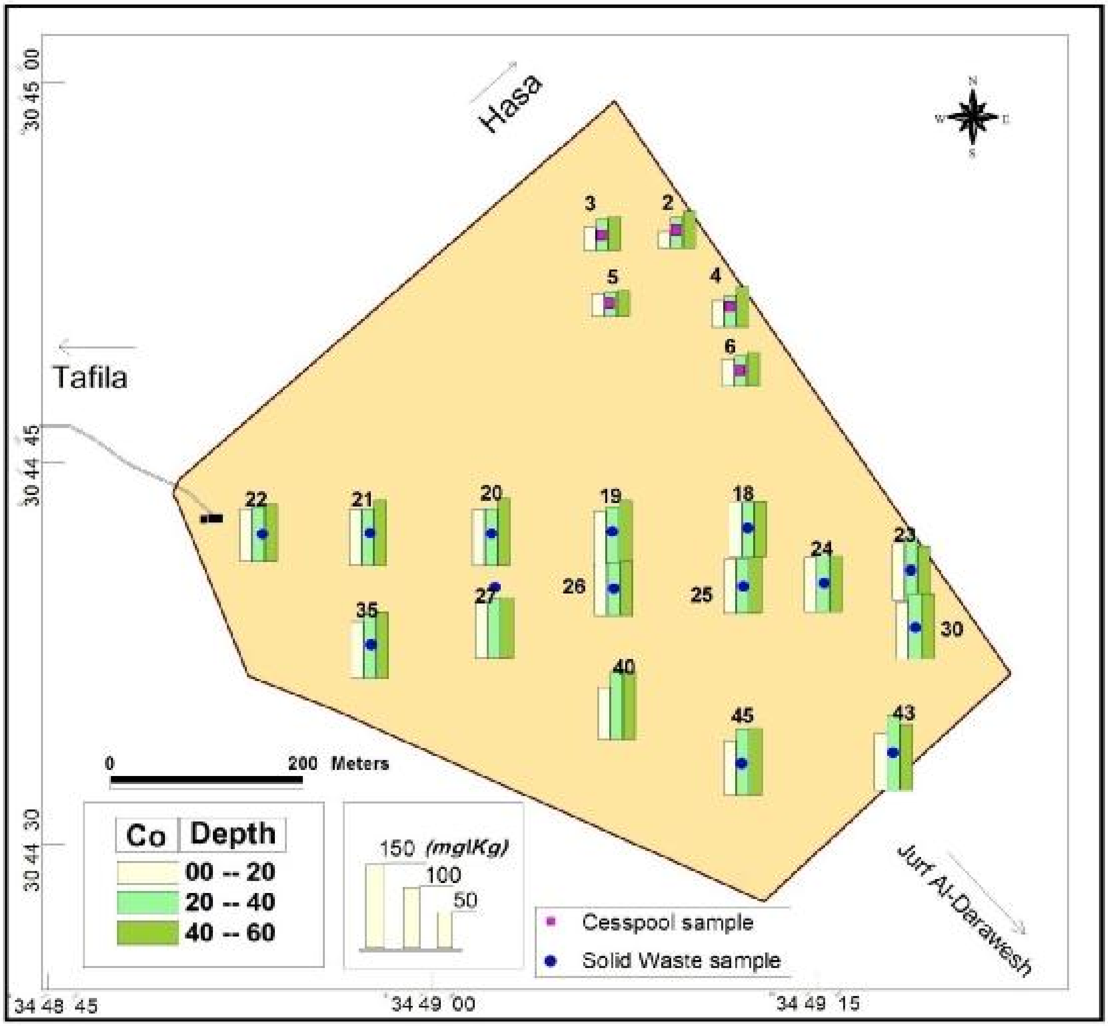


Figure (3.10)
Distribution of Co Concentrations using GIS map at 0-20, 20-40, and 40-60 cm.

3.4.4 Nickel

The concentrations of Nickel (Ni) in soil samples collected from Tafila solid waste disposal site ranged from 81.65 to 272.30 mg kg^{-1} with an average value of 162.31 mg kg^{-1} at depths 0-20 cm which exceeded value for remote control site (72 to 135 mg kg^{-1} with an average of 162.31 mg kg^{-1}). The highest value of Ni found at site 48 and the lowest value at site 35. The Geographic Information System Map (GIS-map) shows the distribution pattern of Ni in the investigated area Figure 3.11. It was noticed that the highest concentration levels of Ni dominated in the western and south - eastern parts of the investigated area. Ni may originate from iron and steel products, microelectronics, mining and smelting for metals alloys, and battery manufacture wastes. The main source of Ni in the investigated area might be due to the metals waste that consisted of 3 % of the input waste at the investigated site. Additionally, it was found that

4.4% of investigated samples were contained concentration levels below the range of Mc Grath et al. (2001). The typical range of trace elements of non- polluted soil is illustrated in Table 3.12. While, 95.6 % of the samples contained concentration levels above that range. The GIS contour map shows the concentrations levels of Ni using the colored map Index which was given in five ranges (80-120, 121-165, 166-210, 211-250, and 251-290) mg kg^{-1}, Figure 3.11.

The concentrations of Nickel in soil samples at 20-40 cm depths exceeded the remote reference site and ranged from 101.54 to 269.81 mg kg^{-1} with an average value of 174.26 mg kg^{-1}, while, it was ranged from 13 to 19 mg kg^{-1} with an average of 16.33 mg kg^{-1} for the remote control area. The highest value of Ni found at site 23 and the lowest value at site 26. The variation in the concentrations of Ni with depths is shown on Figures 3.11 and 3.12. Finally, the concentrations of Nickel was varied between 22 and 35 mg kg^{-1} with an average of 29.33 mg kg^{-1} in the control area at 40-60 cm depths compared to 11.37 and 283.51 mg kg^{-1} with an average of 199.128 mg kg^{-1} in the study area at the same depth. The highest concentration of Ni was found at site 23 and the lowest at site 35. Figure 3.12 shows a significant variation in the concentrations of Ni with soil depths and site.

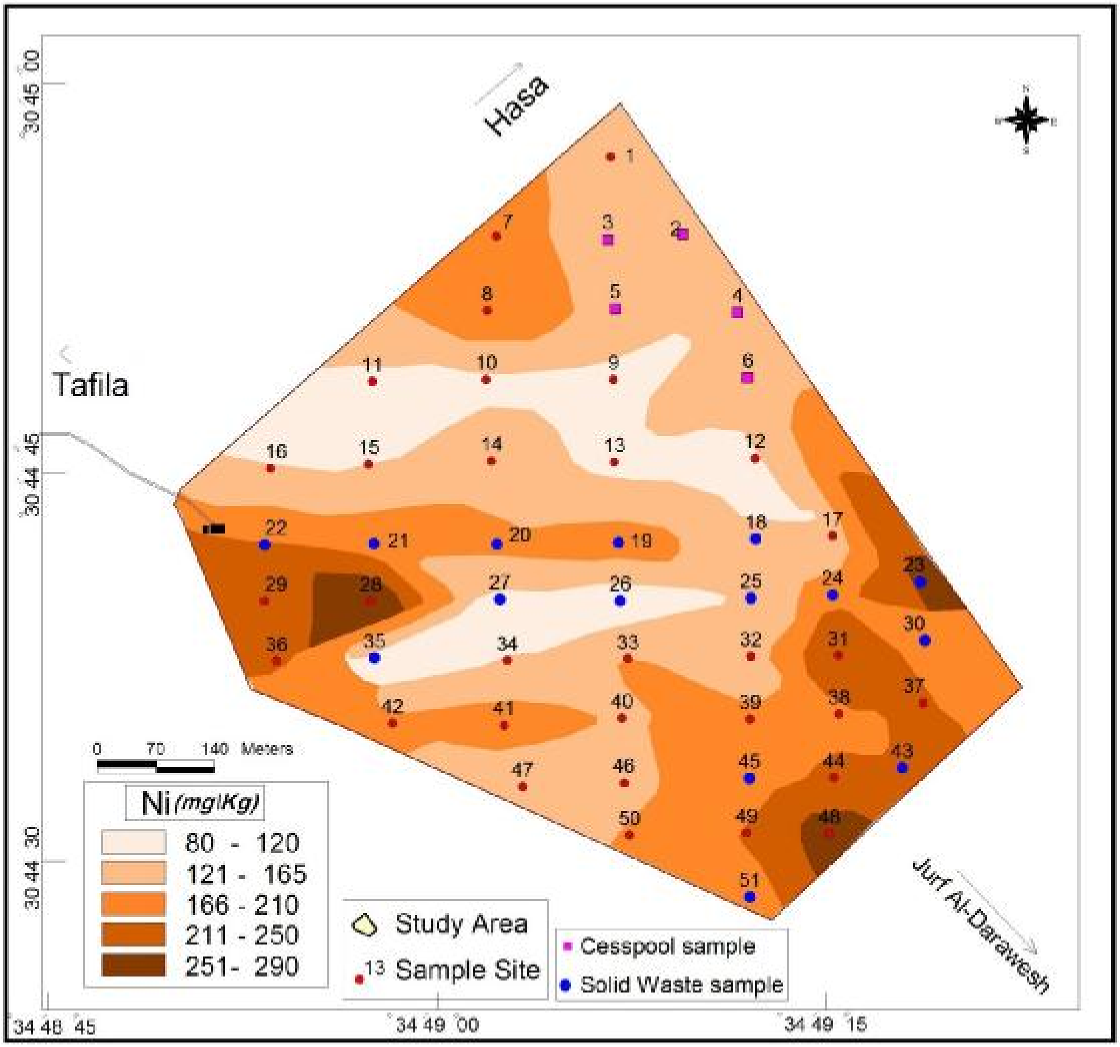


Figure (3.11)
Distribution of Ni Concentrations using GIS map
(0-20 cm).

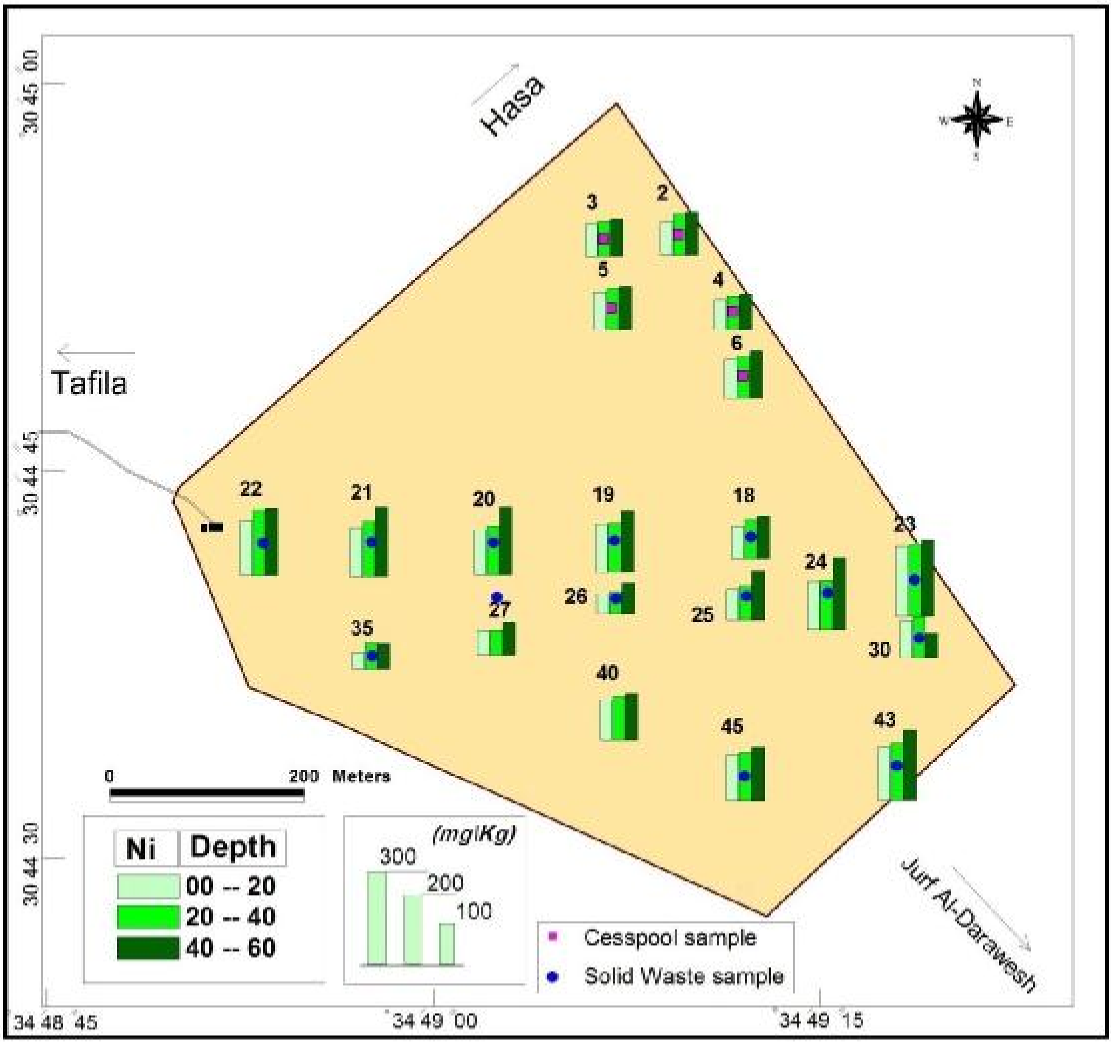


Figure (3.12)
Distribution of Ni Concentrations using GIS map at 0-20,20-40, and 40-60 cm.

3.4.5 Copper

Generally, concentration levels of copper (Cu) in the investigated area were higher than the remote reference site indicating that solid waste disposal activities have been affected the soil quality. The concentrations of Cu in soil samples collected from the Tafila solid waste disposal site ranged from 60 to 280 mg kg^{-1} with an average value of 164.3 mg kg^{-1} at 0-20 depths which exceeded that value for remote control site 20 to 40 mg kg^{-1} with an average of 26.66 mg kg^{-1}. The highest Cu concentration found at sites 15, and 29 and the lowest at sites 17, 39, and 50. The Geographic Information System Map (GIS-map) shows the distribution pattern of Cu in the investigated area, Figure 3.13. The map also shows high variations in Cu concentration levels among the sampling sites but mainly the high concentrations dominated in the western and southeastern parts of the dumping site. Copper may come from mining and smelting of metals,

microelectronics, pesticides waste, automobile waste, fertilizers waste, traffic emission, incineration, manure, wastewater (Wong et al., 1996). Additionally, it was found that 9.9 % of investigated samples contained concentration levels below the range of Mc Grath et al. (2001), which ranged over 2-100 mg kg^{-1}, Table 3.12. While, 90.1 % of the samples contained concentration levels above that range. The GIS contour map shows the concentrations levels of Cu using the colored map index which was given in five ranges (60-105, 106-145, 146-190, 191-240, and 241-280 mg kg^{-1}) Figure 3.13. The concentrations of copper in soil samples at 20-40 cm depths ranged from 100 to 380 mg kg^{-1} with an average value of 184.76 mg kg^{-1}, while, it was ranged from 30 to 70 mg kg^{-1} with an average of 46.66 mg kg^{-1} for the remote control area. The highest value of Cu was found at site 43 and the lowest value at site 24. The variations in the concentrations of Cu metal with depths are shown on Figure 3.14.

Finally, the concentrations of Cu were varied between 50 and 90 mg kg^{-1} with an average of 73.33 mg kg^{-1} in the control area at 40-60 cm depths compared to 140 and 380 mg kg^{-1} with an average of 229.09 mg kg^{-1} in the study area at the same depths. The highest concentration of Cu was found at site 30 and the lowest at site 26. Figure 3.14 shows the significant variation in the concentrations of Cu metals with depths and site.

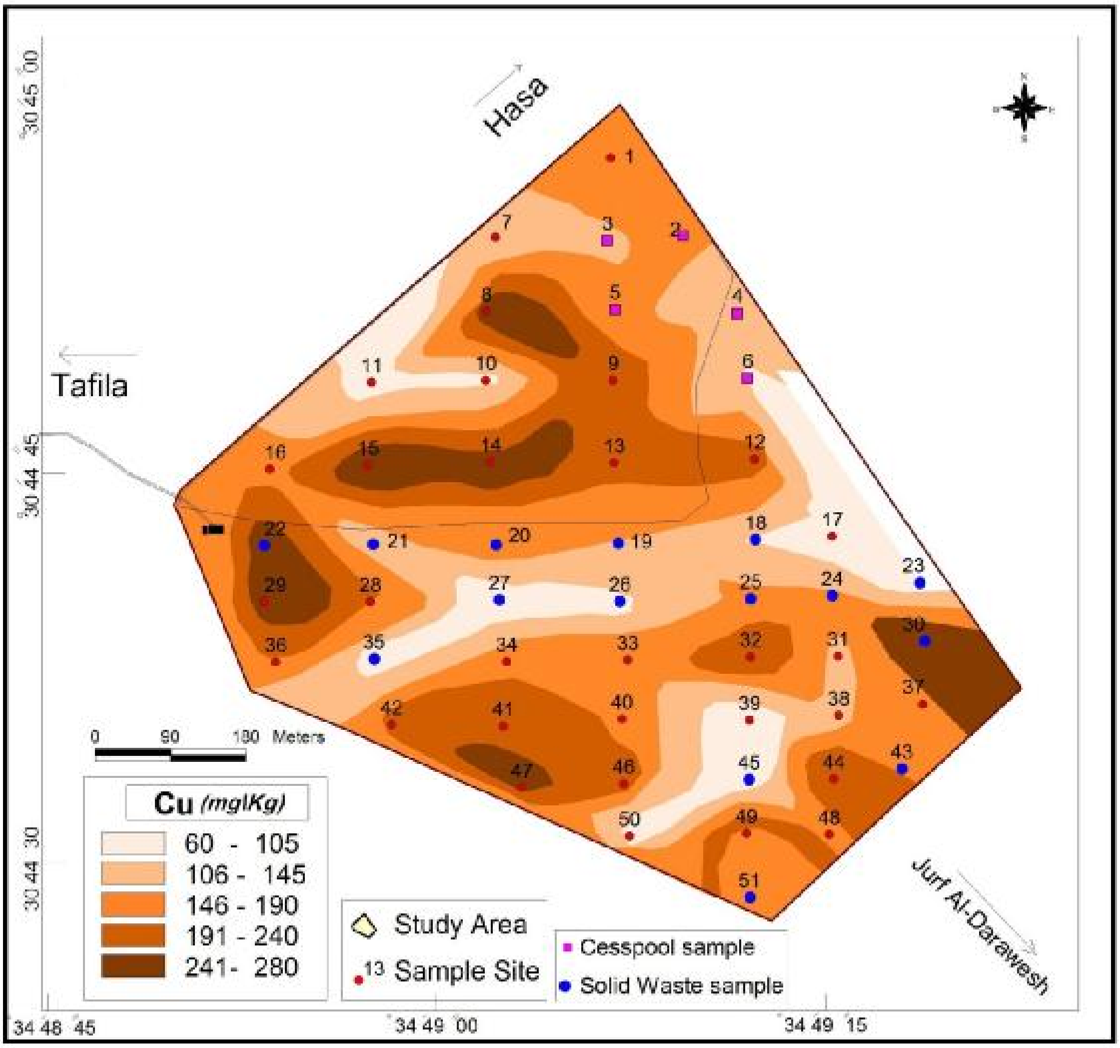


Figure (3.13)
Distribution of Cu Concentrations using GIS map
(0-20 cm).

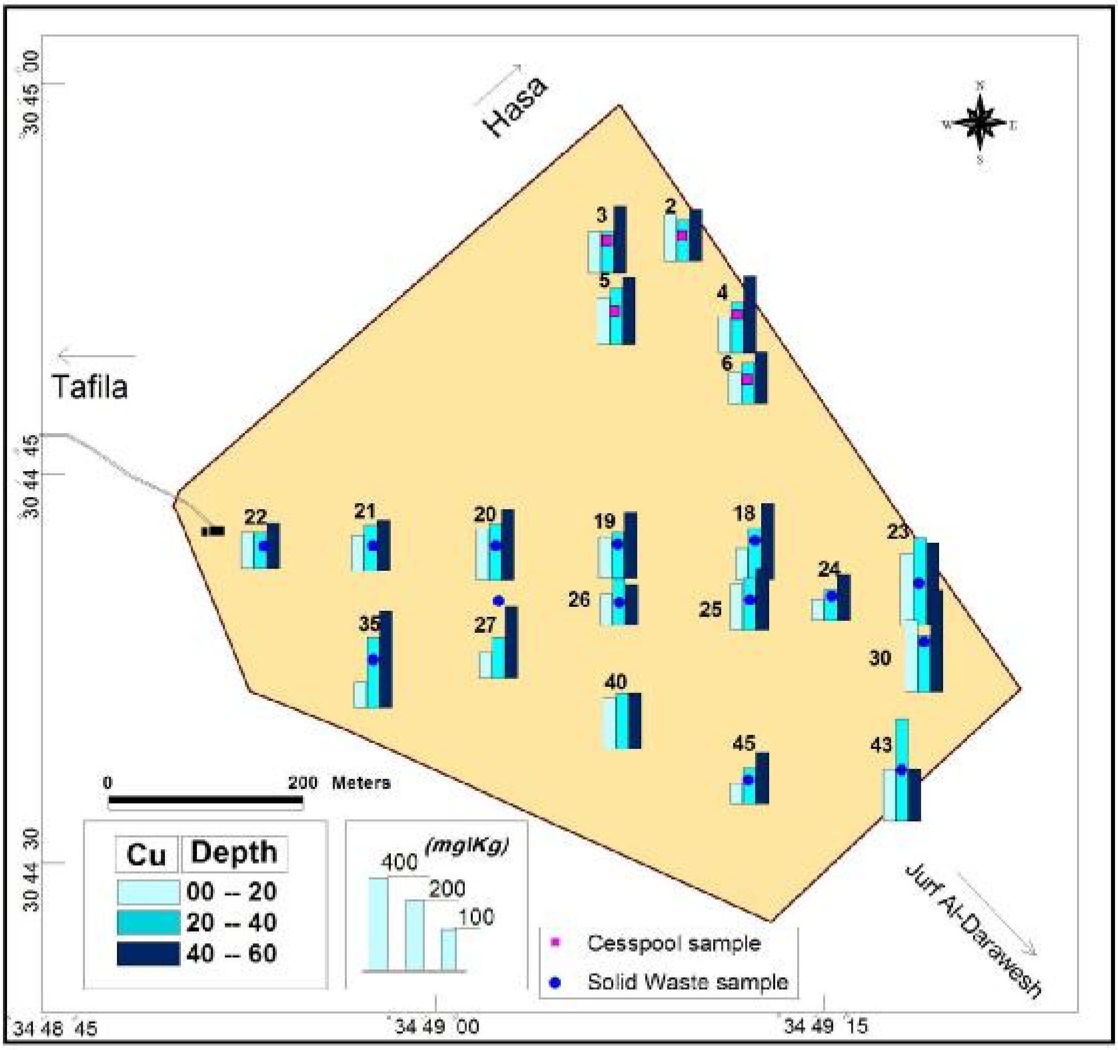


Figure (3.14)
Distribution of Cu Concentrations using GIS map at 0-20, 20-40, and 40-60 cm.

3.4.6 Iron

The concentrations of Iron (Fe) in soil samples collected from the Tafila waste disposal site were ranged from 36 to 312 mg kg^{-1} with an average value of 86.83 mg kg^{-1} at 0-20 depths which exceeding that value for remote control site (72 to 135 mg kg^{-1} with average of 110.66 mg kg^{-1}). The highest Fe concentration was found at site 50 and the lowest at site 25. The Geographic Information System Map (GIS-map) shows the distribution pattern of Fe in the investigated area, Figure (3.15). Where high concentrations dominated only in a small area at the southern part of the dumping site. Iron may come from metallic scraps being co-deposited with domestic wastes; also iron is one of the principle element in the crust and is mainly associated with the coarse atmospheric particles (Berg et al.1995), the GIS contour map shows the concentrations levels of Fe using the colored map Index which was given in five ranges (15-95, 96-170,

171-245, 246-320 ,and 321-400 mg kg^{-1}) Figure 3.15. The concentrations of iron in soil samples at 20-40 cm depths ranged from 24 to 125 mg kg^{-1} with an average value of 67.30 mg kg^{-1}, while, it was ranged from 13 to 19 mg kg^{-1} with an average of 16.33 mg kg^{-1} for the remote control area. The highest value of Fe was found at site 4 and the lowest value at site 21. The variations in the concentrations of Fe metals with depths were shown on Figure 3.16. Finally, the concentrations of iron were varied between 39 and 111 mg kg^{-1} with an average of 75.40 mg kg^{-1} in the control area at 40-60 cm depths compared to 22 and 35 mg kg^{-1} with an average of 29.33 mg kg^{-1} in the study area at the same depths. The highest concentration of Fe was found at site 4 and the lowest at site 35. Figure 3.16 shows a significant variation in the concentrations of Fe metal with soil depths and site.

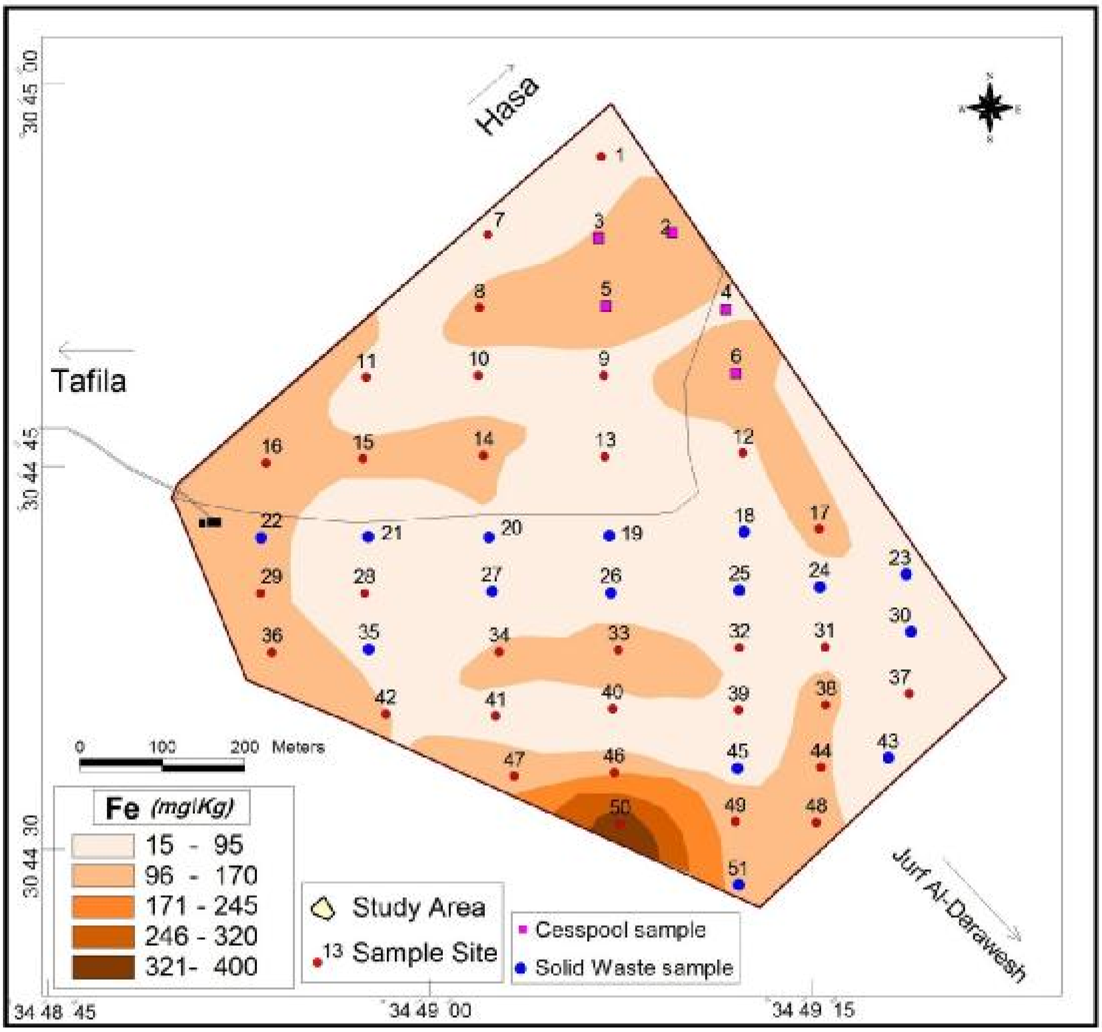


Figure (3.15)
Distribution of Fe Concentrations using GIS map
(0-20 cm).

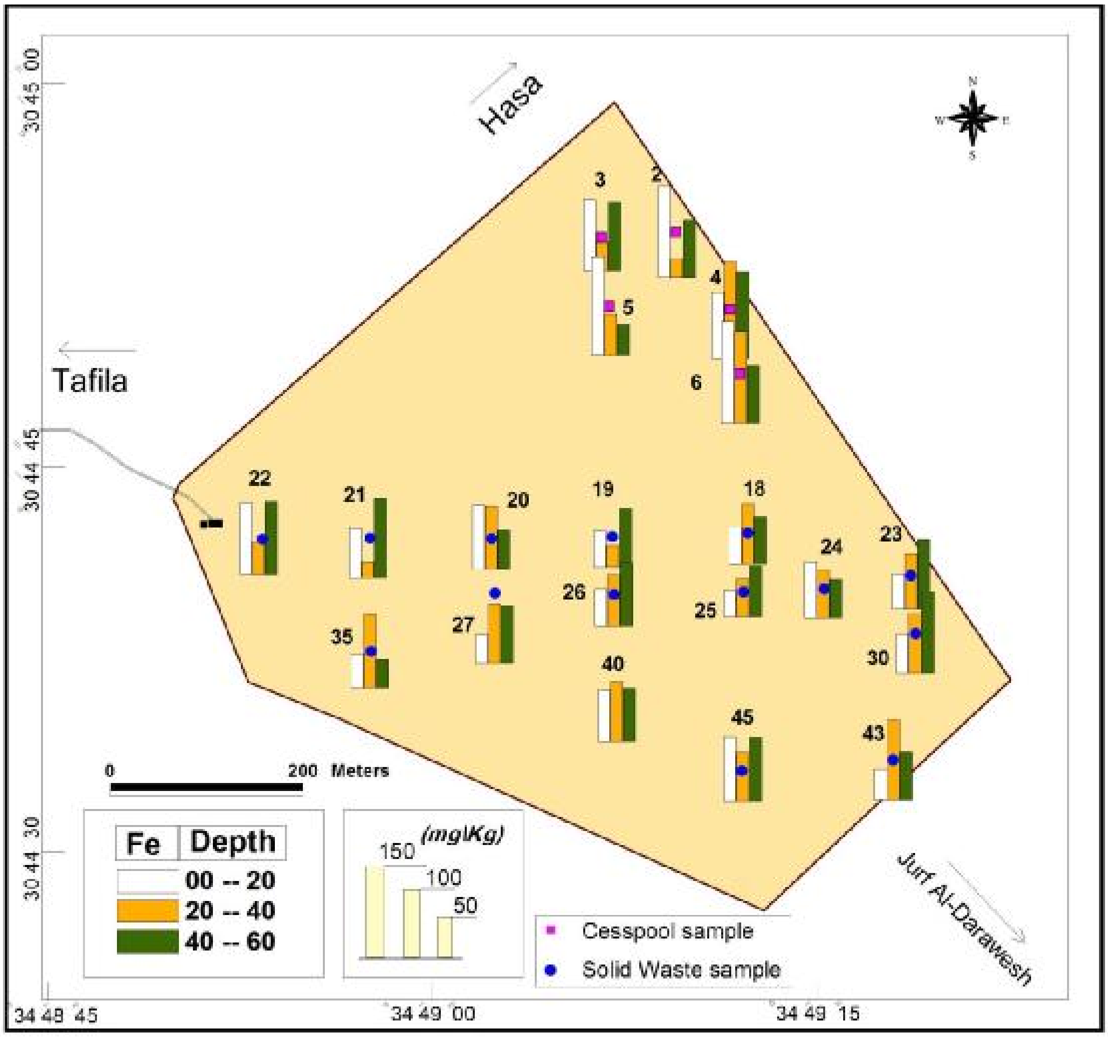


Figure (3.16)
Distribution of Fe using GIS maps at 0-20, 20-40, and 40-60 cm.

Table (3.13)
shows the comparison of trace metals concentration between current study and other studies

Studies	**Zn (mg kg^{-1})**	**Ni (mg kg^{-1})**	**Pb (mg kg^{-1})**	**Cu (mg kg^{-1})**	**Co (mg kg^{-1})**	**Fe (mg kg^{-1})**	**References**
Solid Waste Disposal Site of Thessaloniki (Greece)	6.4 – 343	7 – 64	2.5 – 93	8 – 356	-	-	Kasassi et al. 2008
National Capital Territory of Delhi (India)	116 – 23321	192 – 1534	23- 530	3065 – 10144	-	233 – 684	et al. , Moturi 2004
New Karak Solid Waste Disposal Site	50 - 590	17 - 328	56 - 369	13.7 - 31.2	87 – 181	267-831	Tarawneh, 2012
Old Karak Solid Waste Disposal Site	8433- 21166	-	– 63333 3083	3083 – 6550	-	-	Jiries et al., 1996
Current Study	18 - 395	82 - 272	64 – 285	60 - 280	51 - 104	36 – 312	-

3.5. Correlation between heavy metals:

Table 3.14 shows the correlations between the investigated trace heavy metals in the study area at depth 0-20 cm. While there was no significant correlation between metals, this could means independent source of those metals.

Table (3.14)

Correlation matrices between heavy metals in study area at depth (0-20 cm)

Element	Zn	Ni	Pb	Cu	Fe	Co
Zn	1.000	0.105	-0.213	-0.001	0.322	0.030
Ni	0.105	1.000	-0.290	0.176	0.288	0.183
Pb	-0.213	-0.290	1.000	0.071	-0.345	0.037
Cu	-0.001	0.176	0.071	1.000	0.165	0.185
Fe	0.322	0.288	-0.345	0.165	1.000	-0.146
Co	0.030	0.183	0.037	0.185	-0.146	1.000

Table 3.15 shows the correlation between the investigated trace metals in the study area at depth 20-40 cm. while there were no significant correlation between metals which means they were of independent sources.

Table (3.15)

Correlation matrices between heavy metals in study area at depth (20-40 cm)

Element	Zn	Ni	Pb	Cu	Fe	Co
Zn	1.000	-0.230	0.247	-0.028	0.433	0.068
Ni	-0.230	1.000	0.213	0.231	-0.199	0.209
Pb	0.247	0.213	1.000	-0.105	-0.264	0.360
Cu	-0.028	0.231	-0.105	1.000	0.393	0.257
Fe	0.433	-0.199	-0.264	0.393	1.000	-0.051
Co	0.068	0.209	0.360	0.257	-0.051	1.000

Table 3.16 shows the correlation between the investigated trace metals in the study area at depth 40-60 cm. While there were no significant correlation between the metals. This could mean independent source of those metals.

Table (3.16)

Correlation matrices between heavy metals in study area at depth (40-60 cm)

Element	Zn	Ni	Pb	Cu	Fe	Co
Zn	1.000	-0.129	-0.190	-0.422	0.318	-0.041
Ni	-0.129	1.000	0.112	0.125	-0.131	0.389
Pb	-0.190	0.112	1.000	-0.137	-0.256	0.253
Cu	-0.422	0.125	-0.137	1.000	-0.296	0.133
Fe	0.318	-0.131	-0.256	-0.296	1.000	-0.019
Co	-0.041	0.389	0.253	0.133	-0.019	1.000

3.6 . Correlation between heavy metals and soil properties

Table 3.17 shows the correlation between trace heavy metal concentrations, physical and chemical soil parameters at depth 0-20 cm. It was found significant correlation between Fe and clay %, and Ni and TOC%.

Table (3.17)

Correlation matrices between heavy metals, physical and chemical soil properties at depth (0-20 cm).

Element	Zn	Ni	Pb	Cu	Fe	Co
PH	-0.195	-0.247	-0.225	-0.119	0.088	-0.155
EC	-0.295	-0.281	0.123	0.175	-0.093	0.249
TOC %	0.016	0.558	-0.418	0.128	0.183	-0.044
$CaCO_3$ %	0.423	0.167	-0.267	0.215	-0.057	0.451
Texture (Clay%)	0.188	0.488	-0.402	-0.163	0.726	-0.575

Table 3.18 shows the correlation between heavy metal concentrations, physical and chemical soil parameters at depth 20-40 cm. The results showed that significant correlations between Ni and TOC %, Co and clay %,Co and $CaCO_3$%, Cu and pH, Pb and pH, Pb and EC.

Table (3.18)

Correlation matrices between heavy metals in study area and physical and chemical properties at depth (20-40 cm)

Element	Zn	Ni	Pb	Cu	Fe	Co
pH	0.153	0.089	0.762	0.722	0.050	-0.732
EC	-0.259	-0.083	0.976	0.229	-0.222	-0.353
TOC	-0.518	0.982	-0.429	-0.104	-0.729	-0.535
$CaCO_3$ %	-0.279	-0.186	-0.594	-0.845	-0.123	0.835
Texture (Clay %)	-0.117	-0.526	-0.362	-0.778	0.112	0.977

Table 3.19 shows the correlation between heavy metals concentration and physical and chemical parameters at depth 40-60 cm. There were significant correlation between Pb and EC, Pb and pH, Co and TOC %, Co and $CaCO_3$% , Cu and clay %, Cu and pH, Fe and clay %, Fe and TOC %, Zn and TOC %.

Table (3.19)

Correlation matrices between heavy metals in study area and physical and chemical properties at depth (40-60 cm)

Parameters	Zn	Ni	Pb	Cu	Fe	Co
pH	0.178	-0.803	0.729	0.918	0.319	-0.069
EC	0.455	-0.113	0.956	0.124	-0.238	-0.465
TOC %	0.762	-0.471	-0.259	-0.081	0.870	0.950
$CaCO_3$ %	0.281	0.381	-0.707	-0.774	0.217	0.566
Texture (Clay %)	0.239	-0.971	0.371	0.939	0.683	0.364

3.7. Enrichment factor

Enrichment factor (EF) for trace metals in soil were calculated based on the equation described by Ogunsola et al. (1994).

$EF=[C_X / C_{Fe}]_{soil} / [C_X / C_{Fe}]_{crust}$

$[C_X]_{soil}$= concentration of the element in soil sample

$[C_{Fe}]_{soil}$= concentration of the element Fe in soil sample

$[C_{Fe}]_{crust}$= concentration of the element Fe in earth crust.

Where the concentration of the Fe in the earth crust is (56300 mg/kg) .

Iron was applied as a reference element because it is the most naturally abundant element in soil. It is important to note that the enrichment coefficient is a convenient measure of geochemical trends and is used for comparisons between areas and over time. The enrichment coefficient gives insight into differentiating an anthropogenic source from natural origin (Nolting et al. 1999; Yougming et al. 2006). Five contamination categories were recognized based on enrichment coefficient values (Sutherland, 2000; Loska and Wiechula, 2003), Table 3.20.

Table (3.20)

Contamination categories based on enrichment factor (EF) Value.

Deficiency to minimal enrichment	EF<2
Moderate enrichment	EF=2-5
Significant enrichment	EF=5-20
Very high enrichment	EF=20-40
Extremely high enrichment	EF>40

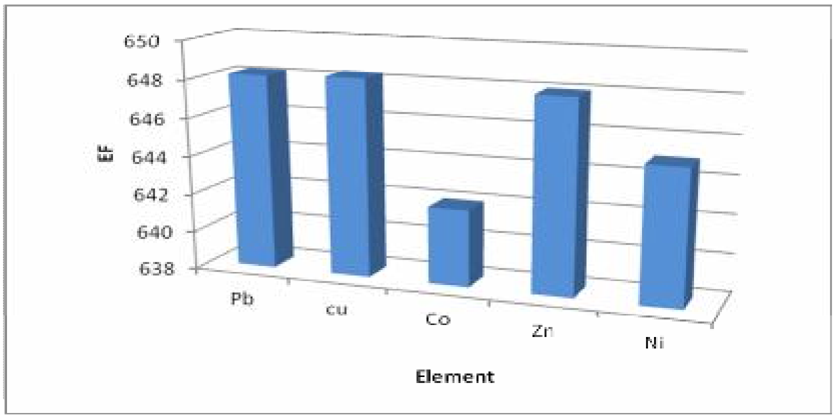


Figure (3.17)

Average enrichment factors of heavy metals in study area

As shown in Figure 3.17 , Co had the lowest EF average value (642), and Zn, Pb, Cu, and Ni have been enriched with EF 648, 648.2, 648.32, and 645, respectively. The order for enrichment factor found as follows: Cu>Pb>Zn>Ni>Co. These metals were considered to originate mainly from anthropogenic sources. When used the concentration of the Fe

in the control study area (110.66 mg kg^{-1}) as shown in figure 3.18 , Zn had the highest EF average value, Ni and Co had the lowest EF average value (1.27), and Zn, Pb, and Cu, have been enriched with EF 1.3, 1.28,and 1.28, respectively. These metals were considered to originate mainly from anthropogenic sources.

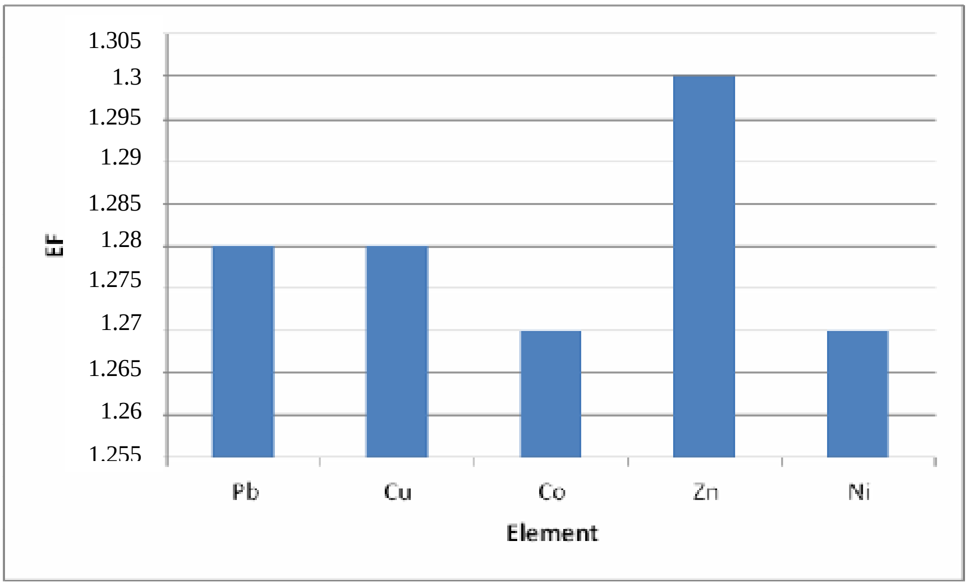


Figure (3.18)
Average enrichment factors of heavy metals in study area

3.8. Statistical analysis

The Principal Component Analysis (PCA) was used to determine the heavy metal distribution trends and their controlling factor in order to identify the potential sources of those metals. The results have been graphically displayed as loading plot for the investigated area. PCA was adopted to assist the interpretation of elemental data. This powerful method allows identifying the different metal groups which correlated to each other. All the statistical analyses were performed using SPSS for Windows (release Ver.13, Inc, Chicago, IL).

Statistical methods can be a strong tool for monitoring of current environmental quality of soils in terms of heavy metal accumulation and for predicating the future soil pollution. The principal component analysis (PCA) is applied to auto scaled data matrix showing the variations between the heavy metals at the soil depths. The variables are correlated with three principle components in which 86.7 % of the total variance in the data is found. These components are related to the sources of trace elements in the soil samples, for 0-20 cm depth the first component with 67.3% of variance comprises Zn, Ni, and Fe with high loading, this association strongly suggests that these variables have a similar source; the source would from solid wastes and wastewater disposal activities. PC2 contributes Cu and Pb at 19.4 % is attributed to other sources such as

automobile exhaust, and traffic movements by car service as sources of heavy metals pollution in the study area, PC3 this component is pooled variable, Figure 3.19 .

For 20-40 cm depths the first component with 58.3 %, and PC2 with 21.3% variance due to contribute of Cu and Fe, and this association strongly suggests that these variables have a similar leaching quantity which contaminant and transferred from a stabilized matrix to liquid medium of heavy metals in the study area, PC3 this component was pooled variable, Figure 3.20.

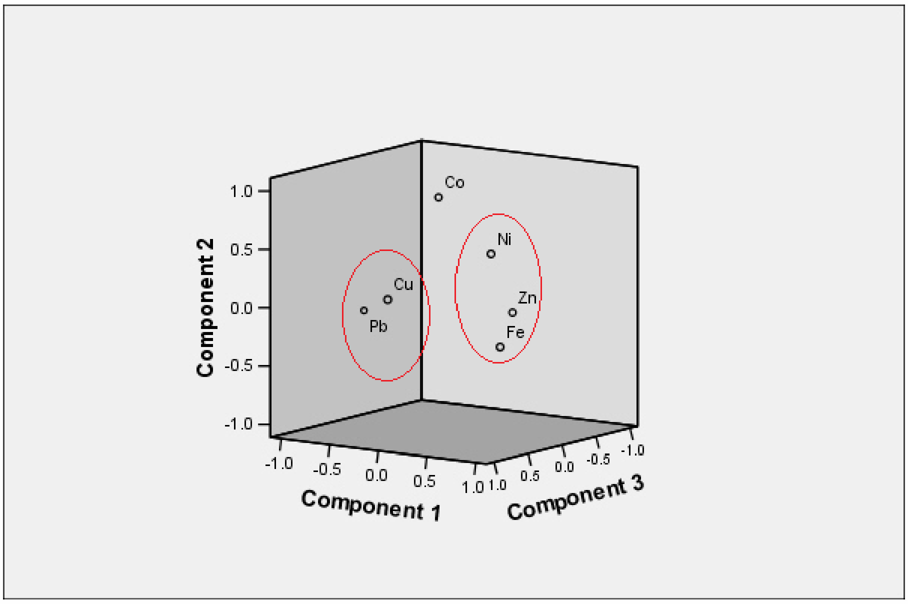


Figure 3.19
Principal component analysis loading plot for rotated components, REGR factor at depth 0-20 cm

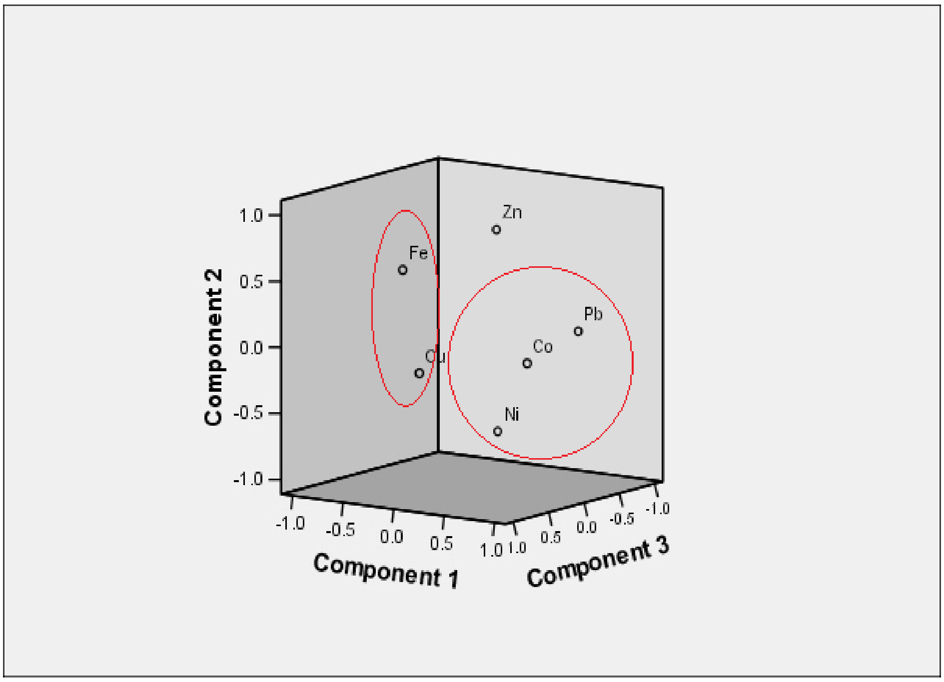


Figure (3.20)

Principal component analysis loading plot for rotated components, REGR factor at depth 20-40 cm

For 40-60 cm depths the first component with 53.58%, PC2 with 23.73 % these variables have a similar leaching quantity which contaminants are transferred from a stabilized matrix to liquid medium of heavy metals in the study area, PC3 this component is pooled variable, Figure (3.21) .

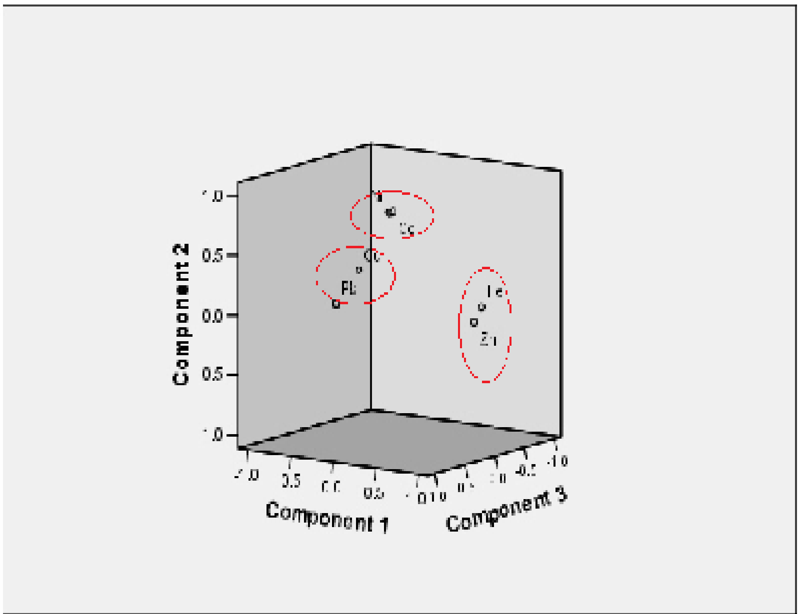


Figure (3.21)

Principal component analysis loading plot for rotated components, REGR factor at depth 40-60 cm

3.9.Conclusions and Recommendations:

The following can be concluded from the present study:

1-Optimization and validation of the analytical method for determination of trace metals using atomic absorption spectroscopy accompanied with microwave digestion. The certified reference material was used for validation parameters including the elements recovery rate, limit of determination (LOD), and limit of quantitation (LOQ).

2- The results of the measured properties such as pH, Total Organic Carbon (TOC %), Electrical Conductivity (EC), calcium carbonate percentage ($CaCO_3$ %) showed that the soils of the study area were moderately basic with high electrical conductivity compared with remote control samples. Additionally, it had high values of TOC % compared to control samples.

3- It was possible to draw GIS contour maps for trace metals to show their distribution pattern in soil profile using GIS mapping techniques.

4- Significant differences in the levels of trace metals were observed between soil samples and control area.

5- Leaching of trace metals through soil profiles is causing the possibility of ground water pollution, especially, when it comes to uncontrolled solid waste disposal with the absence of lining and monitoring systems of the waste received. There was clear a lack in waste management practices, coupled with the rapid increase in solid waste, which poses a negative effect on health and environment.

6- The soil samples of the investigated area can be classified as a loamy soil, from the geological study.

7- The distribution of the metal concentration of the soil in the study area indicated that this area has been affected by solid wastes and cesspools disposal activities which lead to a high accumulation of trace heavy metals in soil of study area.

8. It is recommended to study the impacts of the solid waste disposal site on air quality and groundwater resources.

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